Synthesis of novel ionic liquids for cellulose processing

Master´s Thesis

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Nowadays one main objective in chemistry is to find environmentally benign alternatives to non-biodegradable materials, like common plastics. Further, as fossil resources are decreasing, novel approaches to utilize renewable materials (like biomass), are becoming increasingly important for the mankind. There is a long-standing interest for utilization of cellulose; it is the most abundant polymer on earth and can be found in many organisms such as plant, algae, and bacteria but also in some animal species.

Cellulose is the most abundant biogenic polymer used in the world; its largest source is from wood, which contains up to 50% of cellulose but also other compounds such as lignin (up to 30%), hemicellulose (up to 30%), inorganic salts and proteins.

The main challenge is to dissolve cellulose, because of is strong intra- and intermolecular hydrogen bonding, it is not soluble in common molecular organic solvents and does not melt.

According to these problems of cellulose dissolution, a novel class of solvents has been designed and called: Ionic liquids (ILs). ILs are made of an organic cation and an organic or inorganic anion, their major difference from classic salts is their lower melting point (under 100°C)

They are able to do covalent and ionic bonds as normal organic solvent do, but their special character comes from the fact that ILs are able to do also strong H-bonding and columbic interactions.

The mechanism of the dissolution itself has been studied using molecular dynamics and it has been shown that the anion and cellulose build a strong hydrogen-bonding network between them; the cation has a different stabilizing effect on dissolution as it is dominated by Van der Walls and electrostatic interactions. The structure of the IL plays a big role. A non-hindered cation will be more effective and, an anion with high basicity will be the most effective.

Many of the ILs studied to dissolve cellulose contain phosphonium cations or halogen anions, such combination leads to toxicity and corrosive action against reaction vessels. To diminish the negative effects, other combinations have to be designed. Chemist started to use superbases as a cation and weak acid such as acetic acid as an anion to form superbase-based ILs. ILs-based on guanidine are known to be chemically and thermally stable, this comes from the high proton delocalisation between the three nitrogen atoms.

Even if they are able to dissolve cellulose, their characteristics related to their structure such as high melting point and high viscosity are a problem for lab experiments using a classic magnetic stirring. Also they are limited to 10 wt% cellulose dissolution. A lot of superbase ILs such as immidazolium-based ILs were investigated for cellulose dissolution but they require temperature higher than 90°C enhancing cellulose degradation.

So bicyclic guanidine were investigated as a potential class of ILs. Because of their rigid bicyclic structure, they are less affected by steric effect than their acyclic analogue. This explains why chemists started to be interested in bicyclic guanidine species in ILs such as TBD and its methylated version mTBD.

Avainsanat – Nyckelord – Keywords **cellulose, ionic liquids, superbases**

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List of abbreviations

AA: Acetic Acid

ADV: Acid Digestion Vessel

AGU: Anhydroglucose Unit

$AlCl_3$: Aluminium Chloride

a-TBD: Allyl-TBD

BTM-TBD: Beta-Tetra-Methylated TBD

BTM-mTBD: Beta-Tetra-Methylated mTBD

b-TBD. Butyl-TBD

BF_4^- : Tetrafluoroborate

$Ca(ClO)_2$: Calcium Hypochlorite

CED: cupriethylenediamine

CF_3COOH: Trifluoroacetic acid

CMC: Sodium CarboxyMethyl Cellulose

CP-MAS: Cross Polarization Magic Angle Spinning

Cuam: $Cu(OH)_2/NH_3$

Cadoxen: cadmium ethylenediamine

CS_2: Carbon disulfide

$CSCl_2$: Thiophosgene

DBU: 1,8-DiazaBicyclo(5.4.0)Undec-7-ene

DBN: 1,5-Diazabicyclo(4.3.0)non-5-ene

DEA: Diethylamine

DEC: Diethylcarbonate

DIPA: Diisopropylamine

DMA: Dimethylacetamide

DMAN: 1,8-bis(dimethylamino)naphthalene

DMC: Dimethyl Carbonate

DMF: Dimethylformamide

DMSO: Dimethyl Sulfoxide

DP: Degree of Polymerization

D_2O: Deuterium Oxide

EDCl: 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide

e-TBD: Ethyl- TBD

GPC/SEC: gel permeation and size exclusion chromatography

H_2SO_4: Sulphuric Acid

h-TBD: Hexyl-TBD

IL: Ionic Liquid

IR: Infra-Red

KOH: Potassium Hydroxide

K_2CO_3: Potassium carbonate

$KHCO_3$: Potassium bicarbonate

Lac: Lactic Acid

LDA: Lithium Diisopropylamide

$LiAlH_4$: Lithium Aluminium Hydride

LiCl: Lithium Chloride

MCC: Microcrystalline Cellulose

MeI: Methyl Iodide

m-TBD: Methyl-TBD

NaOH: Sodium Hydroxide

Na_2CO_3: Sodium Carbonate

NMR: Nuclear Magnetic Resonance ~~Spectroscopy~~

$[P_{14666}][Cl]$: trihexyl(tetradecyl)phosphonium

$[P_{4444}][OAc]$: Tetrabutyl Phosphonium Acetate

$[P_{8881}]OAc]$: Trioctylmethylphosphonium Acetate

ppm: Particle Per Minute

PF_6^-: Hexafluorophosphate

RBF: Round Bottom Flask

SO_2: Sulfur Dioxide

TBAF: Tetra-n-butylammonium Fluoride

TBD: Triazabicyclodecene

TGA: Thermogravimetric Analysis

THF: Tetrahydrofuran

TMG: 1,1,3,3-Tetramethylguanidine

t-BuOK : Potassium tert-butoxide

VOC: volatile organic compounds

WAXS: Wide-angle X-ray scattering

1. Introduction

Nowadays one main objective in chemistry is to find environmentally benign alternatives to non-biodegradable materials, like common plastics. Further, as fossil resources are decreasing, novel approaches to utilize renewable materials (like biomass), are becoming increasingly important for the mankind. There is a long-standing interest for utilization of cellulose; it is the most abundant polymer on earth and can be found in many organisms such as plant, algae, and bacteria but also in some animal species. Cellulose consists of glucose molecules bonded together to form a semi rigid polymer. In plants, cellulose usually exists as a structural element, fibre, which is resulting from inter- and intramolecular hydrogen bonding between cellulose molecules. In other words, cellulose is forming a semi crystalline structure of wood's fibrils in the cell walls (Figure 1).[1]

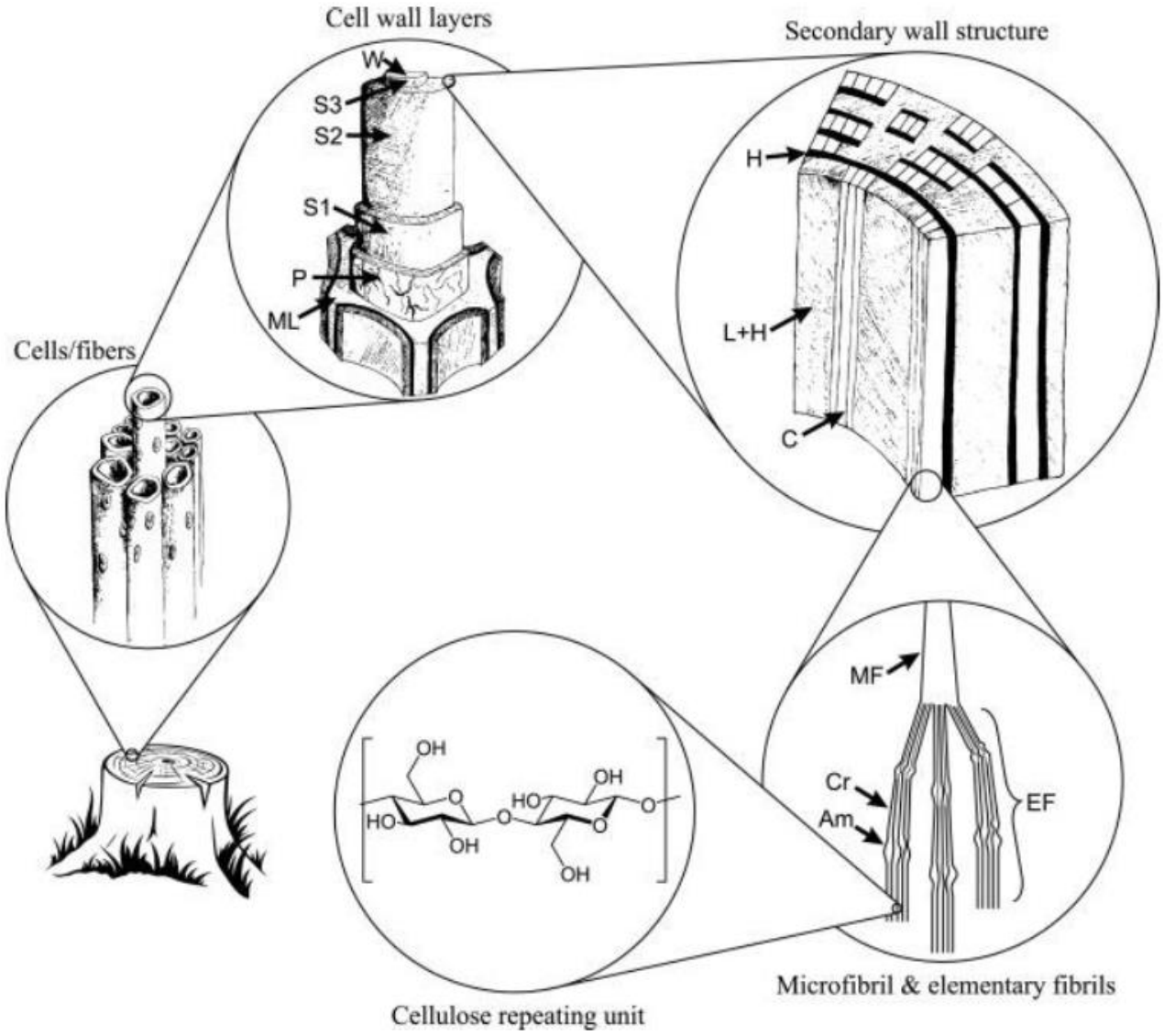


Figure 1. Structure of wood biomass. MF: microfibrils, EF: elementary fibril, Cr: Crystalline region Am: amorphous region[2]

Depending on the plant's species, the length of the polymer (DP, degree of polymerization) and its molecular organisation are different.[1] Today, cellulose has a central role in many everyday commodities, like paper and pulp, clothes (cotton, viscose) and cellulose derivatives (cellulose acetate and CMC).

The natural abundance of cellulose is enormous, estimated to 1.5 trillion tons.[3] Although cellulose has been successfully applied in numerous industrial processes during 19th, 20th 21st centuries, a few

major challenges still remain related to the industrial processing of this material – Cellulose does not dissolve in common organic solvents and does not melt which makes challenges for its efficient processing. To overcome these difficulties, there is a continuous need to develop efficient methods to utilize cellulose as feedstock for different applications.

The insolubility of cellulose is originates from the strong intra- and intermolecular hydrogen bonding network, which is difficult to break.[4,5] Dissolution of cellulose can be achieved if the inter and intra-molecular hydrogen bonds of cellulose are broken and if after this the chain is stabilized by the solvent. However, very few conventional solvent systems possess hydrogen-bonding properties that would favour breakage of the hydrogen bonding networks of cellulose. [4]

According to these problems of cellulose dissolution, a novel class of solvents has been designed and called: Ionic liquids. They are made of an organic cation and an organic or inorganic anion, their major difference from classic salts is their lower melting point (under 100°C). [6] ILs have demonstrated good capacities to dissolve cellulose (more than 15 wt% for some of them) [7] and because of their unlimited possible ionic combinations, they have become one of the major methods of interest to dissolve cellulose. [6] Many of the ILs studied to dissolve cellulose contain phosphonium cations or halogen anions, such combination leads to toxicity and corrosive action against reaction vessels. To diminish the negative effects, other combinations have to be designed. Chemist started to use superbases as a cation and weak acid such as acetic acid as an anion to form superbase-based ILs. Most often, organic superbases contains nitrogen atoms in their structure where a guanidine function has been introduced to the alpha-carbon. [8] These type of ILs contains highly stabilised cations able to form strong hydrogen-bond networks with cellulose because of the free carboxylate anions that are able to interact with the hydroxyl groups present in the glucosidic units.[9]

In the following chapters, cellulose properties and characterization methods are discussed (p.11), followed by different methods for dissolution (p.16). Finally p.45, the experimental work on different ILs.

2. Cellulose

2.1. History

Cellulose is the most abundant biogenic polymer used in the world; its largest source is from wood, which contains up to 50% of cellulose but also other compounds such as lignin (up to 30%), hemicellulose (up to 30%), inorganic salts and proteins.[3] As the cellulose is not the only component of wood, it needs to be extracted i.e. using pulping with reagents such as NaOH, Na_2SO_3 and $Ca(ClO)_2$ at high pressure[10].

The Chinese were the first to use bamboo to make pulp as we know it today. During the Christian era this method was common and started to be developed also in Europe and became the main method to make paper from wood in the 14th century. [11]

Anselme Payen a French chemist, was the first to isolate pure cellulose from plants in 1837. The polymer structure of cellulose started to be accepted by other scientist in the early 1920's .[12] He demonstrated that cellulose is not only used by humans but also by animals, for instance in wasp's nests and also that for each type of plant the amount of cellulose is different.[13]

Since this time, cellulose received a particular interest because of its renewable characteristics, the main problem is its insolubility in inorganic or even organic solvents which affect its exploitation.[14]

In the early 1850's scientists discovered by accident a compound called nitrocellulose, which is an explosive substance later used as gun cotton. Since then, man-made fibres have been more and more studied.[15] Later in 1930, regenerated cellulose came into bulk industrial use through the viscose process. More recently in the 1960s, another type of man-made cellulose fibre appeared using N-methylmorpholine-N-oxide (NMMO) monohydrate as a cellulose solvent.[15] Actually, the NMMO lyocell and the viscose processes are the only approaches used for cellulose dissolution and regeneration in industry. Currently, the NMMO lyocell process is the main alternative to the viscose process but it is also hazardous because of its explosion risk associated with thermal decomposition of NMMO.[15] A new class of solvents called ionic liquids (ILs) appeared to be able to solubilize a large variety of compound such as organic or inorganic molecules but also polymers. Most of them have a low vapour pressure, this particular property was highly interesting for chemical processes.[16] Even if they are regarded as greener than other classic solvents, many of these ILs contain halogen anions which are aggressive for the vessel used in laboratory and several show high toxicity.[17] A lot of

efforts are ongoing to find a way to change the composition of these ILs and to make them harmless towards humans and the environment but also to understand better the mechanism of cellulose dissolution. This point was the motivation for the review and experimental work.

2.2. Structure of cellulose

An intra unit H-bonding system exists between the OH group on the C3 of one glucose molecule and the O5 of another. In addition to this system, the two glucosidic molecules are linked together by a the β 1→4 glycosidic bond. This leads to a more stable linkage and a linear configuration of the polymer (Figure 3). [18] [19]

Cellulose chains have two different endings, one on the C4 is typically referred to a secondary alcohol and called "non-reducing end", the second one is on on the opposite end of the chain, on the C1 and contains a cyclic acetal function referred to " reducing end" (Figure 2).[20]

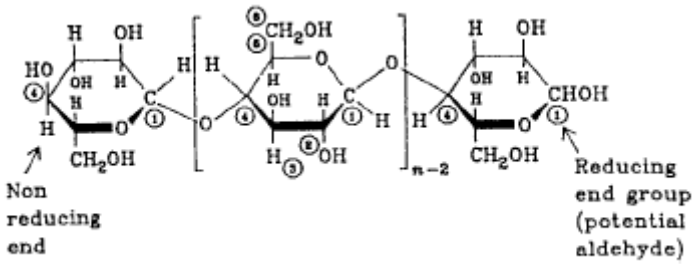


Figure 2. Different units of cellulose[21]

Each unit of the chain contains three hydroxyl group: C2 and C3 are secondary alcohol and C6 is a primary, they play an important role for the reactivity.[22] In the glucose ring, the alcohol functions are in equatorial position according to the ring's plane this corresponds to the chain conformation called "^{4}C1 conformation" (Figure 3).[21] The degree of polymerisation of cellulose can reach 15 000 units, the exact value depends of the cellulose source.[18]

Because of the hydrogen system built due to the presence of hydroxyl groups, cellulose can ends up with a semi crystalline structure and can be classified in different groups: cellulose I, II, III and IV.[23] Cellulose I is called "natural cellulose" because it is produced naturally by trees, algae or bacteria also its structure can converted by mercerization into cellulose II and III.[18] One particularity of cellulose I is that it is actually two different allomorphs I_α and I_β, their proportions depend on the cellulose source. Also, I_α is the major component and can be converted into I_β conformation by

hydrothermal treatment.[19] Cellulose II is the most studied allomorph and can be made by solubilisation then re-precipitation of cellulose I or mercerization (NaOH treatment).[24]

Each allomorph has its own hydrogen-bonding chain orientation and this has an impact on mechanical properties of the material (Figure 3). These crystalline allomorphs can be identified using solid state NMR, IR and WAXS.[25]

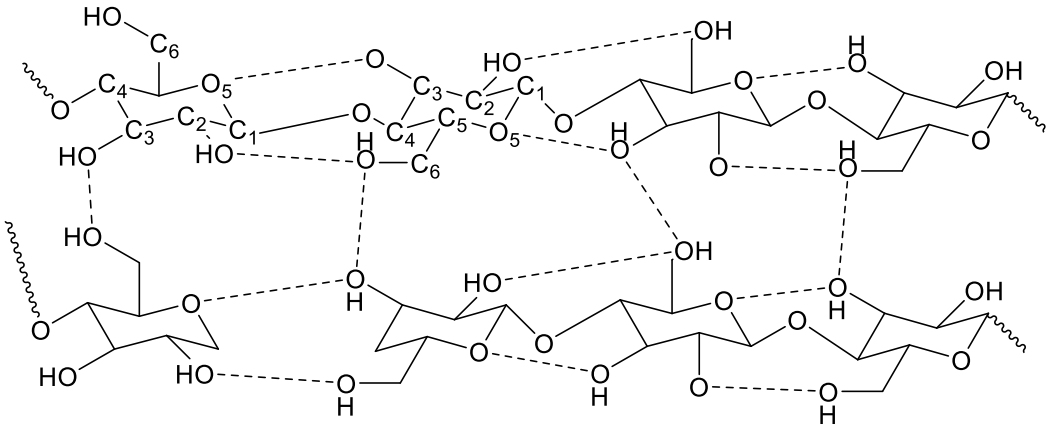


Figure 3.Inter and intramolecular hydrogen network in cellulose

Cellulose molecule (width of 0.4 nm) can be packed into cellulose microfibrils (width of 3-4 nm) which form bundles (at least 15 nm) and lead to cellulose fibre (20 to 30 µm).Elementary fibrils can be divided into two parts: crystalline and amorphous regions (Figure 1).[26]

2.3. Dissolution of cellulose

As said previously, cellulose is not soluble in common molecular solvents. Its monomers are made of glucose which is a molecule which is highly soluble in polar solvents such as water.[27] However cellulose itself is not soluble. This characteristic contrasts to other polyglucose such as dextran, which is soluble in water. [28].Cellulose is described as an amphiphilic polymer, it consists into two segments: one is polar, the other one nonpolar.[27] This characteristic comes from its structure; the hydrophilic property is from the hydroxyl group attached in equatorial position on the glycopyranose rings of the full chain. The hydrophobic character is from the axial hydrogens attached to the rings backbone. This leads to an extension of Van Der Waals and hydrogen—bonding network thus amphiphilic solvents are needed for dissolution.[29]

2.3.1. Thermodynamics of dissolution

Dissolution is a process where two phases mix together to form another homogeneous phase. This comes from a separated phase system; the dissolution is taking place only if the free energy of one-phase system is lower than the initial two phase state.[28]

The capacity of a solvent to dissolve a polymer depends on the free energy of mixing ΔG_{mix}. If the value is negative the dissolution will occur spontaneously. When the energy is highly positive, a heterogeneous system made of two phases is formed.

$$\Delta Gmix = \Delta Hmix - TSmix$$

Equation 1. Expression of Gibbs free energy

Polymer size plays an important role in the dissolution process. by increasing its molecular weight it decreases the entropic term and leads to a bigger role of the enthalpy. This explains why polymers are more difficult to dissolve than macromolecules.[30] As stated above, to dissolve a polymer the solvent must be able to overcome the intramolecular interactions in the polymer (mainly hydrogen-bonding and Van der Waals). In a good solvent the polymer will able to change its conformation and this will increase its entropy, on the other hand the solvent will order its molecules so its entropy will decrease.[31] Thermodynamic data on cellulose dissolution are difficult to attain and very little is in the literature.

2.3.2. Swelling of cellulose

Once in contact with the solvent, cellulosic fibres (pulp fibres) can behave in five different ways called “modes” (Figure 4):

- Mode 1: The dissolution is fast and the cellulose disintegrates into fragments. This requires a very good solvent, no swelling is observable.
- Mode 2: Cellulose swells by a phenomenon called “ballooning” and dissolves after. This is made by using a moderate solvent, the balloons will burst and this will lead to dissolution of cellulose.
- Mode 3: Swelling is still happening and balloons appear but with no dissolution. In this case, a bad solvent is used but at least some parts of the cellulose fibres dissolve.
- Mode 4: Homogeneous swelling is observable but no dissolution occurs.

- Mode 5: No swelling or dissolution happens, there is no interaction at all with cellulose.[32,33]

Swelling of native cellulose plays an important role in cellulose chemistry. This phenomena is important for chemical reactivity of pulp. Without this, reactions will occur on the surface layer of cellulose only.[34,35] During swelling the solvent penetrates into the fibre through a semi-permeable membrane, the reactants are absorbed into cavity called a "balloon". This phenomenon happens in 4 phases:

- Phase 1: The solvent goes inside the chain and increases its volume, the balloon is formed.
- Phase 2: the critical point of expansion is reached and the balloon burst, the cellulose solution that was contained in it is released. After this the solvent has to dissolved the unswollen part of the fibres and the membrane residues.
- Phase 3: In this step there is no swelling, the dissolution occurs first on the top layer of the unswollen sections.
- Phase 4: the membrane residues are dissolved in this last step.[32]

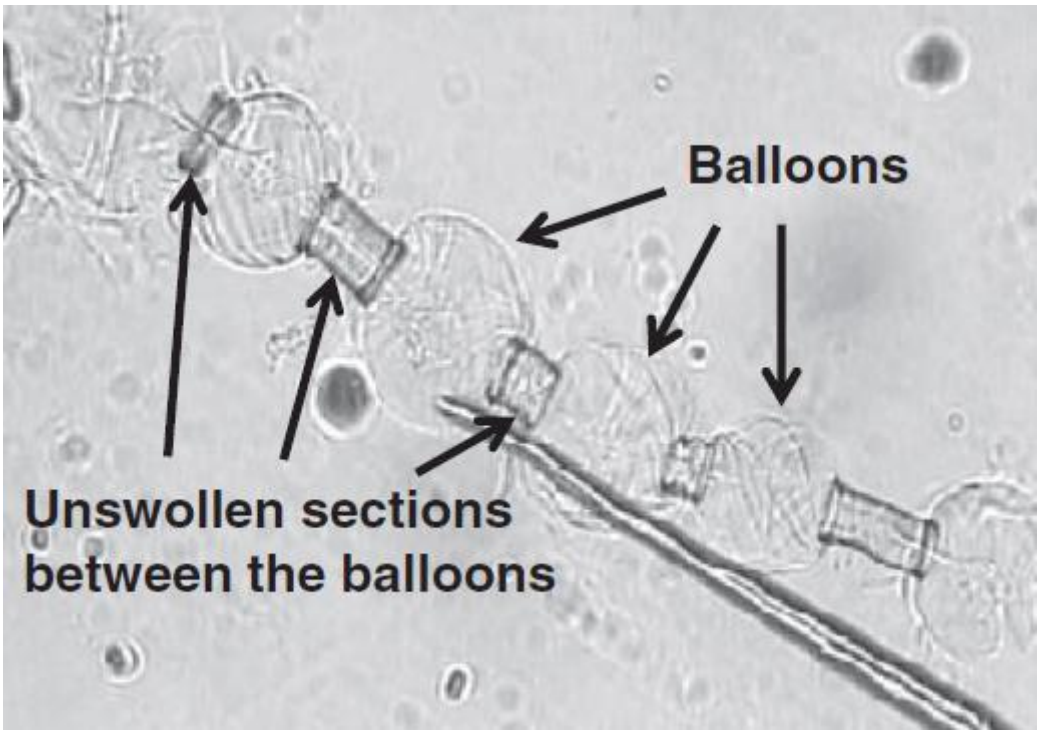


Figure 4. Cellulose swelling and formation of balloons.[32]

Swelling and dissolution are two different reactions with different mechanisms but similarities can be observed.[35]

During the dissolution, the supramolecular structure of cellulose is destroyed; this is observable by the transition of a biphasic system to a one-phase environment. Dissolution of cellulose occurs at the most accessible part of the cell where there is a lower kinetic barrier. This leads to a visible swelling of different regions.[36] If a solvent is not good enough to dissolve cellulose it is suggested that non-crystalline regions swells.

In the chemical reaction, the solvent plays a major role; it activates the reaction by modifying the physical structure of the cellulose by dissolution or by swelling. In a second step the reagent will be able to interact will the cellulose after penetration into the fibre .[35]

2.4. Different types of cellulose solvents

The first efforts to dissolve cellulose were started 150 years ag. Since then, a number of different solvent systems capable of dissolving cellulose have been developed. The first popular categorisation of cellulose solvents appeared in 1980 by Turbak. It was based on the type of interactions between cellulose and solvent:[37]

- Cellulose behaves as a base and the solvent used is an acid such as H_2SO_4 or CF_3COOH.
- Cellulose acts as an acid and the solvent is a base such as KOH.
- Cellulose is used as a ligand and the solvent is a complexing agent, such as cuam or cadoxen.
- Cellulose reacts with the solvent to give a cellulose derivative such as cellulose xanthate.

Later, a chemist called Philip modified this classification. He divided the solvents into different families: derivatizing, non-derivatizing, aqueous and non-aqueous solvents (Figure 5). [37]

A non-derivatizing solvent interacts with cellulose only via non-covalent interactions such as hydrogen-bonds. Unlikely, derivatizing solvents form covalent bonds with cellulose (i.e. cellulose acetal). Later from this reaction, cellulose can be regenerated by decomposition of these cellulose derivatives typically with acidic or alkaline conditions. [38] Thus, some derivatives may be more or less labile. A new classification is proposed based on this (Figure 5).

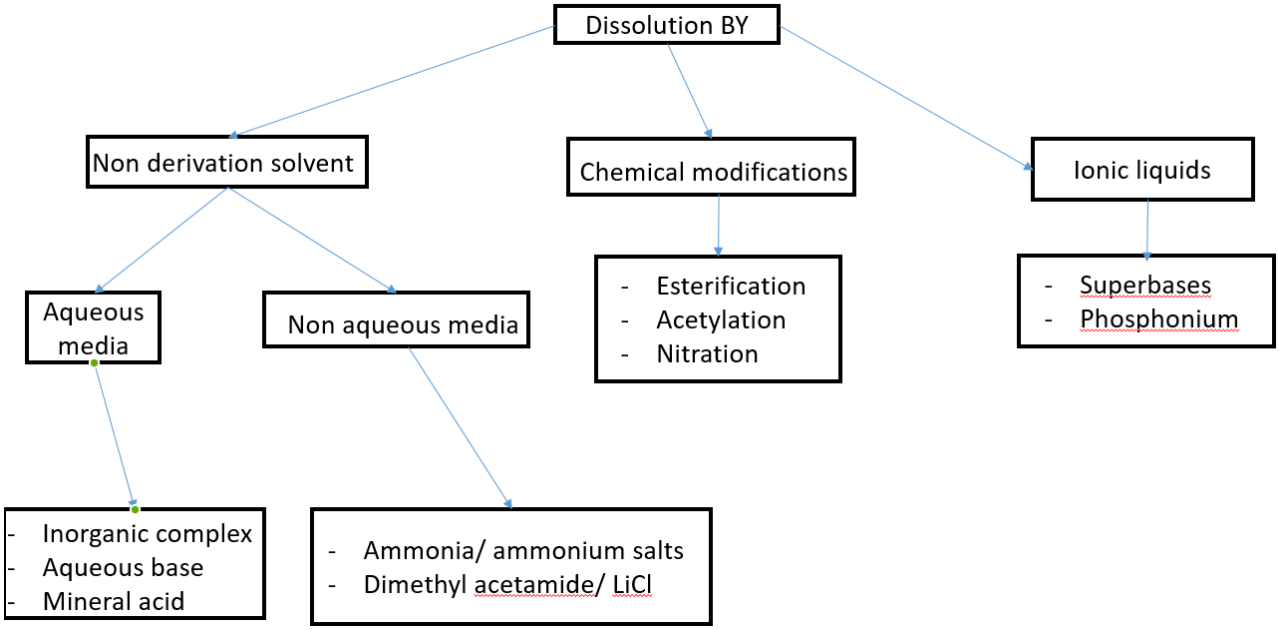


Figure 5. Classification of the main cellulose solvents used adapted from previous classification.

2.4.1. Derivatizing solvents

Chemical modifications occurs mainly by functionalization of the hydroxyl groups present on glucose units. The solvent and the reagent have to break the hydrogen-bonding network of cellulose without depolymerizing the chain. This process is well studied for esterification, nitration or etherification. The solubility of these cellulose derivatives depend on its DP and on the nature of the new functionality itself. Most of the time the cellulose derivatives are soluble in classical dipolar polar aprotic solvents such as DMSO or DMF but poorly soluble in water.[39]

2.4.1.1. Cellulose nitrate

Cellulose nitrate (Figure 6) was discovered in 1845 by a Swiss chemist Christian Friedrich Schoenbein when by coincidence, he mixed a solution of HNO_3/H_2SO_4 with cotton. Once dried, it exploded.[37] After its discovery, cellulose nitrate was used in gunpowder, and later in the late 19th and early 20th centuries was used to produce movie film.[40]

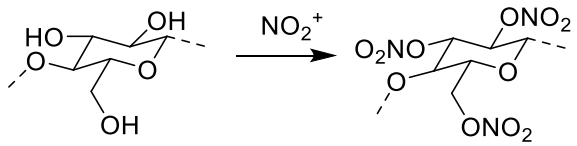


Figure 6. Structure of cellulose nitrate

2.4.1.2. Cellulose xanthate

Cellulose xanthate (Figure 7) results from the treatment of cellulose with sodium hydroxide and then carbon disulphide, it is an important intermediate in the formation of viscose, used to make fibres, films and sponges.[41] Cellulose can be regenerated using acid treatment and heating .[41,42]

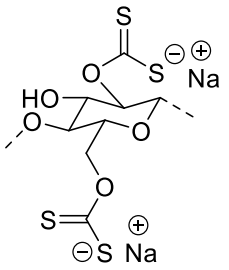


Figure 7. Structure of cellulose xanthate

2.4.1.3. Sodium carboxymethyl cellulose

Sodium carboxymethyl cellulose (CMC, Figure 8) is produced by reacting cellulose with sodium chloroacetate.

This reaction gives an anionic cellulose derivative which is soluble in water. It founded its major application in food chemistry as a thickener i.e. in production of in cheese or frozen yogurt.[43] The viscosity of the solution is temperature dependent if viscosity needs to be decreased.

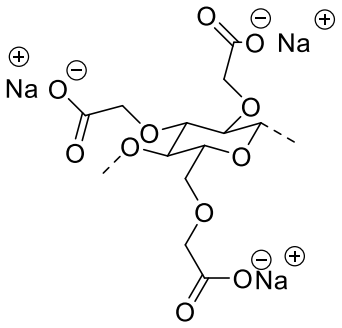


Figure 8. Structure of sodium carboxymethyl cellulose

2.4.1.4. Cellulose acetate

Cellulose acetate (Figure 9) is produced by acetylation of cellulose with acetic anhydride in the presence of acid catalyst, such as sulphuric acid.[44] Among the derivatized celluloses, cellulose acetate is the most widely used one in industry. It is used in textile fibres, plastics or even in photographic films.[44]

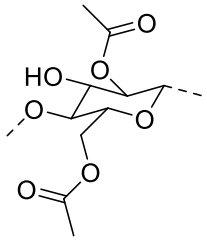


Figure 9. Structure of cellulose acetate

2.4.2. Non-derivatizing solvents

Non-derivatizing solvents are a class of solvents that dissolve cellulose without any chemical modification other than H-bonding and Van der Waals interactions.

In recent years many solvents of this type have been investigated but only a few specialised structures are able to dissolve cellulose without unwanted side reactions, or resulting into gel consistencies.[45] A non-derivatizing solvent can be made of one or more components such as electrolytes which are usually salts dissolution in dipolar aprotic solvents. [45]

2.4.2.1. Aqueous solvents

The first successful dissolution of cellulose with a labile derivatizing solvent system was reported by Schweizer, he used a solution of inorganic salts (cupric hydroxide in aqueous ammonia) to coordinatively bind the deprotonated hydroxyl group in C2 and C3 position of AGU (Figure 10).[46] This solution is the best known solvent in this category, the related CED solution is commonly used for pulp molecular weight determination by intrinsic viscosity measurements .[38]

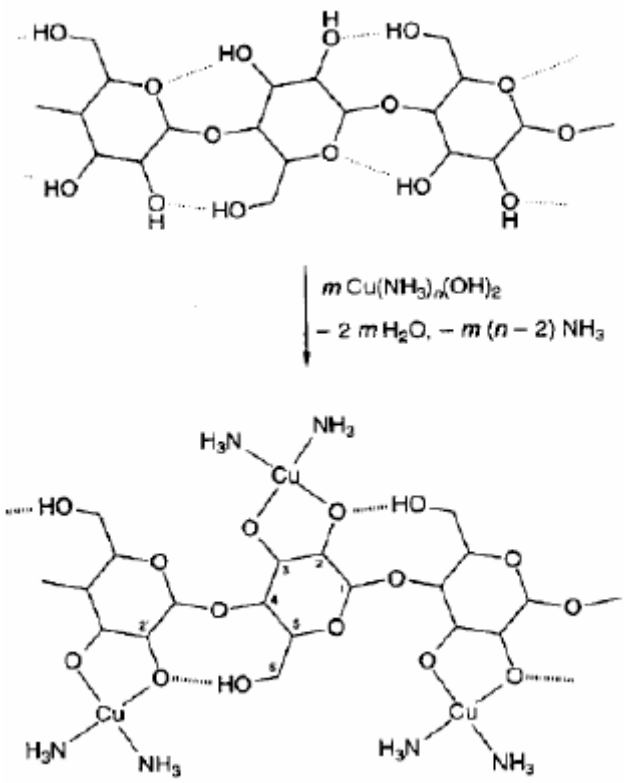


Figure 10. Representation of the Cuam-cellulose interaction. A part of the hydrogen-bonding system changes because of the binding between the copper and the oxygen in C2 and C3.The hydrogen bond between the oxygen in C6 and the cyclic oxygen from the adjacent AGU remains.[46]

2.4.2.2. Non aqueous solvents

LiCl/DMA

This solvent system consistsof dimethyl acetamide (DMA) and LiCl. It is able to dissolve cellulose with a high DP and found application in analytical process of cellulose such as molecular weight distribution determination as a mobile phase for GPC/SEC.[38] It has been reported that also other polar aprotic solvents, such as DMF or DMSO can be used together with LiCl instead of DMA (Figure 11).[47]

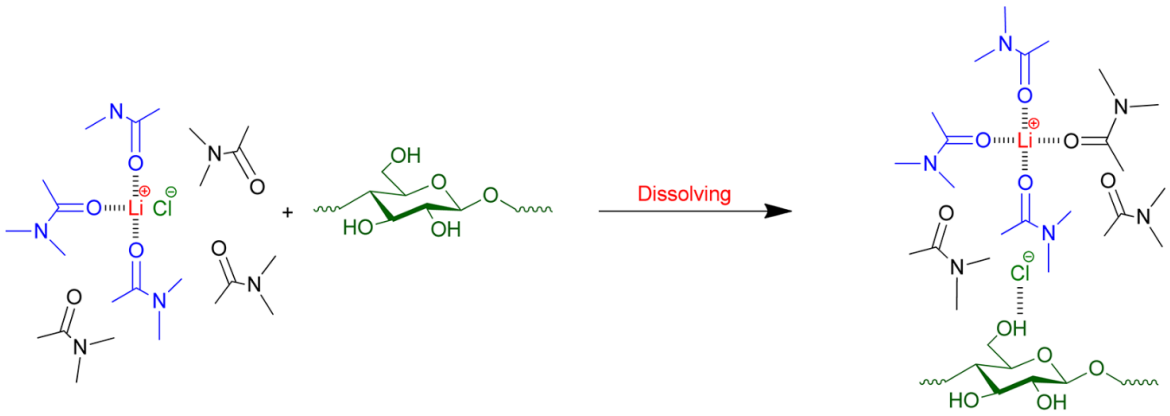


Figure 11. Mechanism of cellulose dissolution in (DMA)/LiCl [48]

2.4.2.3. Other non-aqueous solvents

Numerous non-aqueous solvent systems for dissolution of cellulose have been reported;[30] many of them consist of organic solvent, SO_2 and primary, secondary or tertiary amine. A lot of mixture can be done but the most used is the DMSO/SO_2/DEA[38,49] (Figure 12). It is used as a solvent for cellulose esterification.[49]

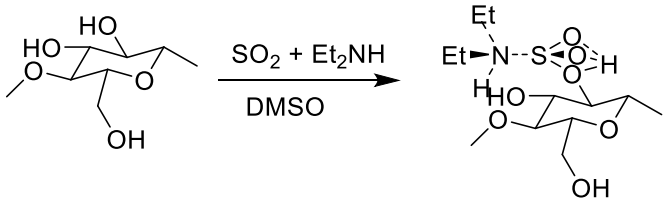


Figure 12. Esterification of cellulose using a mixture of DMSO/SO_2/DEA

2.4.2.4. Ionic liquids

2.4.2.4.1. Phosphonium based ionic liquids

Ionic liquids are another type of non-aqueous solvent system, they are used in many other organic reactions but they can also be applied for cellulose dissolution. Phosphonium-based ILs are able to dissolve cellulose in the presence of a cosolvent such as DMSO. Their high hydrophobicity makes them able to phase separate from an aqueous solution, which is an interesting characteristic for ILs recycled and cellulose regeneration. One inconvenience of this type of IL is the high cost of the phosphonium cation and their potential toxicity, depending on the length of its alkyl chain.[7] (Figure 13)

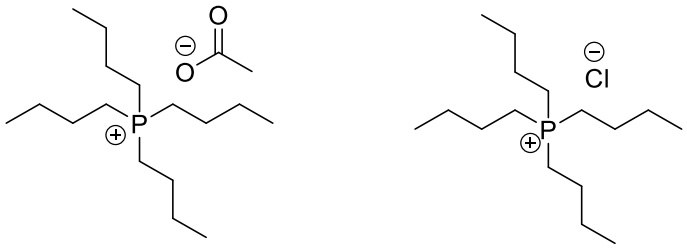


Figure 13. [P_{4444}][OAc] and [P_{4444}][Cl]

2.4.2.4.2. Superbase based ionic liquids

To find an alternative to phosphonium based ILs toxicity[7] a new type of ILs appeared using the conjugated acid of superbases. TMG and DBN based ILs are able to dissolve cellulose up to 15% but can also be distilled at much lower temperature than phosphonium ILs under vacuum. One inconvenient from these two structures is their high viscosity; this parameter is temperature dependant can be a problem for cellulose dissolution.[7] (Figure 14)

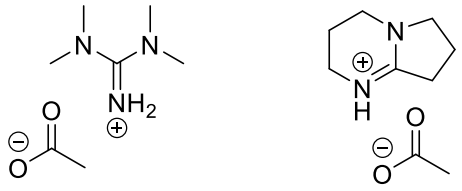


Figure 14. [TMG][OAc] and [DBNH][OAc]

Despite their potential to dissolve cellulose, all these solvents have different limitations, such as toxicity, high cost, environmental hazard and unstability. Due to these limitations, researchers have been eagerly investigating novel, more environmentally benign and financially feasible methods for dissolution of cellulose. Much attention has been paid to the development of ionic liquids for cellulose processes.

3. Characteristics of Ionic liquids

Green Chemistry is a concept developed to introduce more environmental friendly chemistry. For a decade the major issue of this movement is to find alternatives to hazardous species.[50] Most of chemicals organic reactions can be harmful for the environment so risks have to be reduced to an acceptable level. This can be achieved, for example, by changing the chemicals used to less harmful ones or by using less volatile compounds to reduce VOC emissions. These objectives may be achieved by using ionic liquids (ILs).[5] By definition the melting point of an IL has to be lower than

100°C to separate them from normal molten salts such as NaCl, which has a melting point higher of 801°C.[51]

Their properties are related to a complex interphase of Columbic and Van der Waals interactions but also with hydrogen bonding.[52] ILs researches initiated in 1914 with the discovery of ethylammonium nitrate by Paul Walden. Over the past 10 years, more than 10 000 reports have been published about ionic liquids (Figure 15). This initial interest came from their potential as green alternatives to classical organic solvents. ILs are non-volatile under normal pressure, which leads to non-flammability and reduction of the risks of exposure due to inhalation.[53] IL's also have the capability of dissolving various chemicals and materials, (e.g. cellulose), which are difficult to dissolve with conventional organic solvents.

Most ILs are made of an organic cation and an organic or inorganic anion. The number of potential combinations is infinitely large and each can lead to different physico-chemical properties.[6]

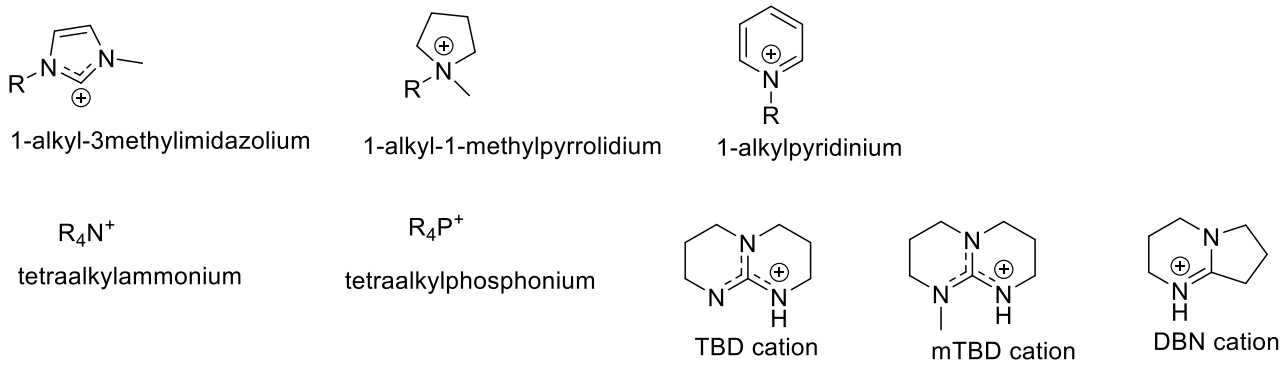


Figure 15. Different cations and anions used in ILs commonly used in ILs.[54]

In 1980's US Force Academy was using LiCL-KCL salts in their batteries, but its high melting point involved high heating, which damaged their batteries. To solve this problem, they started to study ILs.[55,56] Later in the 1980's, Evans worked on ethylammonium nitrate and highlighted that this IL can be used as an non-aqueous environment for biochemical systems and showed the importance of its hydrogen bond system.[57] One year later a chemist called Colin Poole studied this same IL as a stationary phase for gas chromatography, this is how ILs started to be investigated for analytical chemistry and initiated in industrial commercialisation. [54,58]

Nowadays, ILs are investigated in organic reactions as new types of tuneable reaction solvent. The first demonstration of this application was made by Jaeger and Tucker in 1989, using ethylammonium nitrate as a solvent for reactions that had previously been conducted in water.[54,59]

3.1. Physical properties

ILs are able to do covalent and ionic bonds as normal organic solvent do, but their special character comes from the fact that they are able to do also strong H-bonding and columbic interactions.[60]

The bonding interactions occurring in different ILs make their properties different for each ILs, a small change in the structure of the cation such as variation of the alkyl chain length can have a large effect on the physical properties, such as melting point, viscosity and density. The structure of the anion also plays a big role, as it often dictates the basicity and potential for H-bonds formation.[60]

3.1.1. Viscosity of ILs

In general, ILs are much more viscous than classic organic solvents and can even be compared to honey in viscosity.[61] This results from the strong columbic and H-bonds interactions. This can be a problem during reactions as mass transport is low and stirring was not effective. Fortunately, the viscosity of ILs decreases when heated. For example, 1-butyl-3-methylimidazolium hexafluorophosphate's viscosity decreases 27% when heated from 19°C to 25°C. Another way to decrease the viscosity would be to mix with the IL a second solvent but this involves flammability and decrease chemical and electrochemical stability.[62]

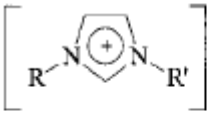
3.1.2. Vapour pressure

One of the most remarkable properties of ILs is their negligible vapour pressure. This can be illustrated by comparing to water which has a vapour pressure of 3kPa at 25°C. The ionic liquid $[C_4mim][PF_6]$ has a vapour pressure of 100kPa at 25°C. It means that a IL can be liquid at room temperature but still not evaporate even under high vacuum. For this reason, ILs are safer to use than conventional organic solvents that can release toxic and flammable fumes. [61]

3.1.3. Melting point

Ionic liquids are different from classical salts because of their melting point; generally, ILs melt below 100°C and some are liquid at room temperature.[63] Not all the ILs have low melting points, but usually low melting points are sought after when a novel ionic liquid is developed. As an example, $AlCl_3$ commonly used in Fridel and Craft reactions, has a melting point around 200°C: This is close to the

boiling point of certain organic solvents, which makes the use of liquid $AlCl_3$ impossible in most applications (Table 1). It has been demonstrated that complexing $AlCL_3$ with chloride ILs will decrease the melting point significantly.[64] The length of the alkyl chain attached to the cation also plays a role. For instance the 1-(C_n)-3-methylimidazolium crystallises only if n=1 or >9.[63] The anion also has an impact on the melting point, for higher homologues of the same anion type, the melting point will typically decrease.[65] The interactions between the two ions is also significant, the weaker they are (dominated by charge-charge interactions or weak Hydrogen-bonds) the lower will be the melting point. This can be explained by reducing the number of conformers available for strong interactions to ordering.[66]

Salt		M. p. [°C]
NaCl		803
KCl		772
	R = R′ = methyl ([MMIM]Cl)[a]	125
	R = methyl, R′ = ethyl ([EMIM]Cl)	87
	R = methyl, R′ = *n*-butyl ([BMIM]Cl)	65

[a] MMIM = 1,3-dimethylimidazolium.

Table 1. This table demonstrates the impact of the cations on the melting point with the same anion.[65]

3.1.4. Thermal stability

Thermal stability of a solvent is often considered as a highly important property for industrial applicability. A low stability will decrease the ILs applicability and can lead to formation of corrosive and toxic side products. In industry, experiments are often done at high temperature so it is needed to determine at which temperature the IL will decompose before using it.[67] As ILs have negligible vapour pressure, their temperature limit is defined by their decomposition temperature (T_d). This parameter is determined by thermogravimetric analysis (TGA). A sample is placed in an inert atmosphere; the heating is increased in a continuous way (typically around 10°C.min^{-1}). The weight loss of the sample is followed; which represents the formation of volatile compounds extracted by a gas flow.

Phosphonium ILs appeared to be highly stable with a decomposition temperature around 250-400°C [68]. Even if they are stable at high temperature, they can still be toxic and it is necessary to find

alternatives. [69] Immidazolium where compared to phosphonium,, are less stable (decomposition temperature around 300°C). Thermal cleavage of a C-N bond can be observed, from attach of the anion. Immidazolium ring itself willstart to decompose around 500°C.[70] As more stable ILs are needed, superbase based ILs started to be studied with the method and were shown to have a temperature decomposition range from 300°C to 380°C. Bicyclic guanidine cations such as [m-TBD] or [b-TBD] demonstrated higher thermal stability than other common cations. [71]

Most of the ILs have a T_d values around 400°C, depending on their structure (Table 2).[72]

Cations		Anions	
	$[C_4mim]^+$	Hexafluorophosphate	PF_6^-
		Tetrafluoroborate	BF_4^-
		Halides	Cl^-, I^-
	$[C_6mim]^+$	Bis(triflylmethyl-sulfonyl)imide $N(SO_2CF_3)_2^-$	Tf_2N^-
	$[C_8mim]^+$		

Table 2. Cations and anions used to study the difference of decomposition temperature between different ILs. This table is present to illustrate the structure of the ILs used in Table 3.[72]

Ionic liquid	Temp. onset for decomposition/°C (dried)
$[C_4mim][Cl]$	254
$[C_4mim][I]$	265
$[C_4mim][BF_4]$	403
$[C_4mim][PF_6]$	349
$[C_4mim][Tf_2N]$	439
$[C_6mim][Cl]$	253
$[C_6mim][PF_6]$	417
$[C_8mim][Cl]$	243
$[C_8mim][PF_6]$	376
$[C_2mim][Cl]$	285
$[C_2mim][I]$	303
$[C_2mim][PF_6]$	375
$[C_2mim][BF_4]$	412
$[C_2mim][Tf_2N]$	455
$[C_2mim][Tf_2N]$	~440
$[C_2mim][CF_3COO]$	~150
$[C_2mim][CF_3SO_3]$	~440
$[C_3mim][Cl]$	282
$[C_3mim][PF_6]$	335
$[C_3mim][Tf_2N]$	452
$[C_4mim][BF_4]$	360
$[C_{18}mim][BF_4]$	360

Table 3. Comparison of different decomposition temperature of ILs as a function of the anion species.[72]

3.1.5. Hydrolytic stability

Because of their desirable properties, ILs are finding application in industry, leading to higher risk of finding contamination of ILs in the environment. Sometimes the decomposition product from reaction between the IL and water is more toxic than the starting material.[73] As a consequence, it is crucial to understand how water interacts with the IL and how it affects its properties. The most unstable ILs anions are the ones containing the $[PF_6]^-$ anion. Once hydrolysed they release HF which is volatile and very corrosive.[73] The nature of the functional group contained in the IL can

help to predict the percentage of hydrolysis i.e. anions with a short chain are more sensitive to hydrolysis compared to the one with longer chains.[74] Some alkylammonium based ILs also demonstrate low stability in water, imidazolium and phosphonium based ILs, in this case are interesting alternatives.[75]

3.1.6. Polarity

Polarity is often a single value describing short and long range transient and slow interactions resulting from charged species. Columbic, dipolar or Van der Waal interactions and hydrogen bonding are included in this concept.[76] Several polarity scales exist for classical organic solvents, such as kinetic rate constant, dielectric constant or some solubility parameters.[77] The most common method to predict an IL behaviour is to use Kamlet Taft parameterisation. This predicts the hydrogen bond donation and acceptor ability in a given solvent type.[78] They can help to understand how the IL will affect the rate and the selectivity of a reaction as well as cellulose dissolution capability. [76] [79]

3.2. Ionic liquids used as cellulose solvent

In 1934, Charles Graenacher made the first publication of cellulose dissolution using molten salts.[80] He used pyridinium-based ILs with chloride as anion. Later in 2002, Swatloski published a paper where he used 1-butyl-3-methylimidazolium-based ILs with different anions (chloride was the most effective anion) for cellulose dissolution. From this publication, the interest in using ILs as cellulose solvent has increased dramatically.[81]

Another type of ILs called room temperature ILs (RTILs), such as 1-ethyl-3-methylimidazolium dimethylphosphate ([emim] [Me_2PO_4]) was also investigated This IL was particularly interesting because of its low viscosity, which leads to faster dissolution and are easier to handle.[7] After this, many ILs have been studied. Resulting from this, it appeared that imidazolium cation and acetate anion was the most effective combination for cellulose dissolution.[82] The mechanism of the dissolution itself has been studied using molecular dynamics and it has been shown that the anion and cellulose build a strong hydrogen-bonding network between them; the cation has a different stabilizing effect on dissolution as it is dominated by Van der Walls and electrostatic interactions. The structure of the IL plays a big role. A non-hindered cation will be more effective and, an anion with high basicity will be the most effective. (Figure 16).[82,83]

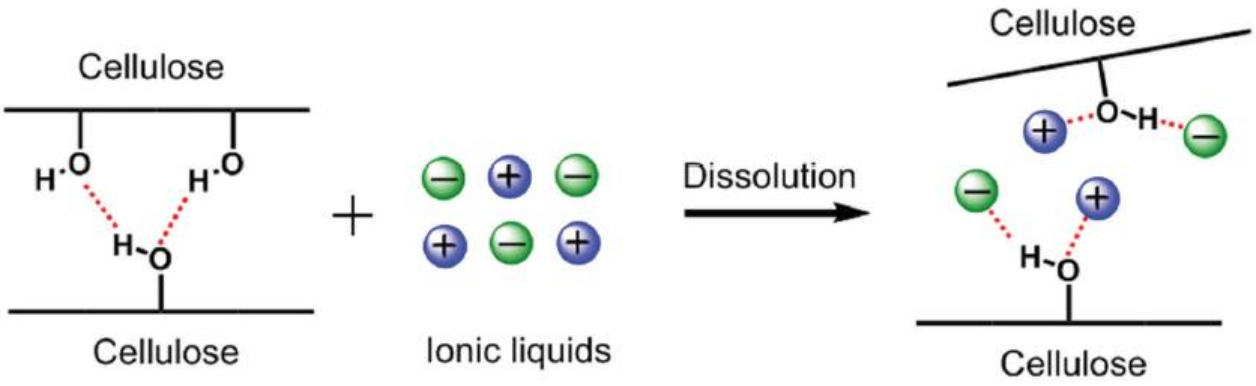


Figure 16. Mechanism of cellulose dissolution using ILs.[84]

In 2014 a study made by Holding and co-authors showed that addition of a polar aprotic solvent such as DMSO helped the dissolution. [7] To obtain a maximum degree of cellulose solubility, the IL has to be as dry as possible because the presence of water will create competitive hydrogen-bonding between water and cellulose and leads to lower solubility. This the case for N-methylmorpholine N-Oxide (NMNO) the monohydrate is the optimum amount of water but a large excess will render cellulose insoluble.[85]

3.3. Toxicity of ILs

One of the potential applications of ILs is to replace VOCs with the aim of decreasing the amount of solvent vaporisation to the atmosphere.[86] This substitution can be possible because of their high thermal stability and low volatility. This is an advantage in a synthetic point of view but it can be also an inconvenient if released in water. Due to their solubility and stability in water, they can be retained and can act as a pollutant .[87] As a consequence, in 2004 Walid H.Awad published a paper where he explains how it is possible to clean-up ILs using oxidative degradation. The products obtained were hydrocarbons, water and CO_2.[88]

During the same year, M.T Garcia and co-authors tried to find another alternative to purify water from ILs: They studied the biodegradability of imidazolium-based ILs using bacterias. He demonstrated that changing the structure of the cation will affect the biodegradability of the ILs i.e. using esterification.[89]

Another inconvenience of imidazolium based ILs is their high absorption in soil due to its structure: the aromatic system leads to a high electron's delocalisation and high electron-acceptor network leading to stronger absorption.[87]

Phosphonium based ILs are more convenient to prepare than immidazolium, they are more stable and their salt synthesis requires shorter reaction time. Their structure makes them resistant against certain nucleophilic attacks. They are also more stable in basic environments.[90] The main issue is the non-biodegradability of these ILs; they are too toxic for the microorganisms in charge of biodegradation.[90]

Also some ILs are not only toxic for environment or biological systems, but they can also be corrosive for reaction vessels. As an example, G.Wytze Meindersma reported that [bmim][I_3] was too corrosive to use it in his experiments. He pointed also the formation of a strong acid: HF from [bmim][PF_6]. In general, halides are the most corrosive of all anions.[91]

A high number of ILs with various structures can be designed. Even if most of them are described as "green solvents" and considered as non-toxic species, some of them can be hazardous. During the following years, studies have been focusing into finding an alternative to the most common archetypical ILs; from this a new generation of ILs called: Protic ionic liquids (PILs) appeared. PILs are made of a conjugated base (A^-) from an acid (AH) and conjugated acid from an organic superbase (BH^+) which exchange proton from the acid to the base.[92,93] A superbase differs from an ordinary organic base by the pKa value of its conjugated acid (BH^+); for a superbase the value will be between 21 and 30 in acetonitrile or between 13 and 16 in water.[92] This type of IL, especially DBN-based ILs have demonstrated higher cellulose dissolution capacities and higher stability than other well-known ILs, this specific family of ILs is described more in details in the following chapter.

4. Guanidines

4.1. History

In organic chemistry, a base is a compound able to free a proton and form a carbanion. In many textbook, organosuperbases are made of amino-groups. Normally this type of function is defined as weakly basic so to increase this basicity it is possible to add an imine group on the α-carbon of the initial amine. Two types of organosuperbase containing amine can be described:[8]

- Amidine: one amine and one imine function, this give a basicity similar to carboxylic esters.

- Guanidine: one amine and two imine functions with a basicity comparable to ortho-esters (Figure 17).[8]

Figure 17. Difference in amidine and guanidine function

The basicity of these compounds depends on the electron resonance system between the nitrogen atoms, if this number increases the system and the basicity also increase, this explains why guanidines are more basic than amidine (Figure 18). [8] The laboratory work was conducted only on guanidines due to their higher basicity and stability, so this literature revue will be also focus only on guanidines.

Guanidines can be found naturally in amino acids such as guanine or arginine, they can also be synthetized and have biological activities. This type of superbase finds applications as antibacterial, hypertensive or antidiabetic. In organic chemistry, they can be used in dehydrohalogenation or aldol condensation. [94]

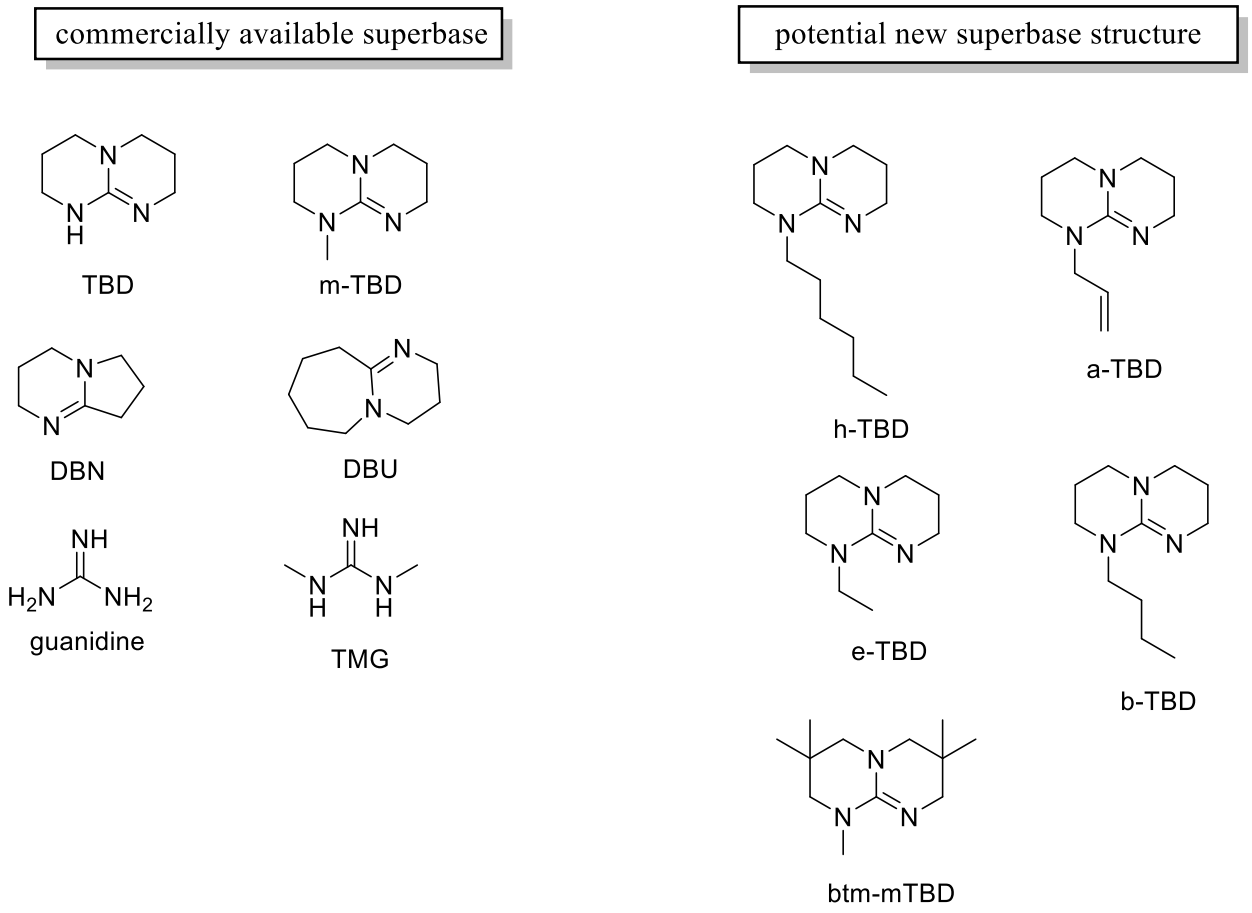


Figure 18. Table of different types of superbases.

In 1968, Alder studied a compound called DMAN made of a naphthalene skeleton and two methylamino function in peri position (Figure 19). This was described as a weak base but it demonstrated high proton affinity. DMAN is called “proton sponge” and used as a reference to compare superbase´s basicity.[95]

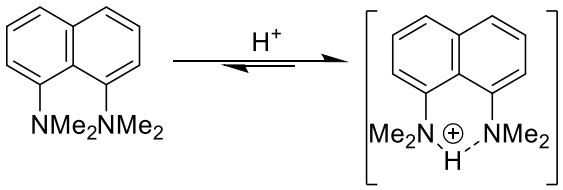


Figure 19. Chelation of DMAN

The name “superbase” can be misunderstood, the term “super” doesn’t mean that a base is stronger than another one but it means that the compound combines characteristics from different bases; for example a new specie combining characteristics from two different amines leading to new

properties (Figure 20). Later in 1985, Schwesinger introduced a new category of superbase made of phosphorus atom attached to four nitrogen functions. Their basicity depends on the number of triaminoiminophosphorane units in the molecule and can reach a basicity of similar to organolithium.[8]

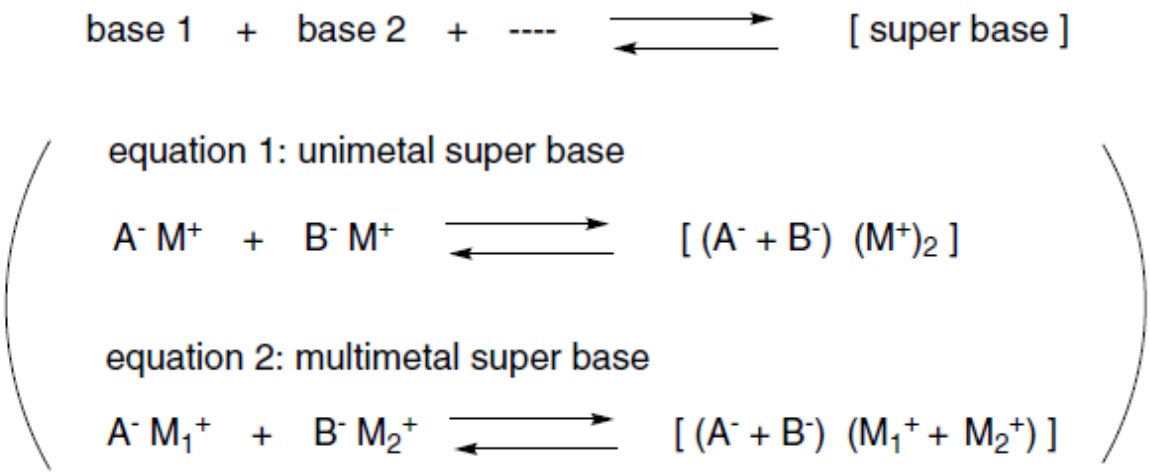


Figure 20. Equation describing the properties of superbase according to Caubère.[8]

4.2. Physico-chemical properties of Guanidines

Classic pH analysis in water using NaOH as a reference cannot not be applied to superbase (pKa of 13,6 in water) so these compounds are compared between each other using a method called gas phase basicity and compared to DMAN. [96] This characteristic developed their use as basic catalyst because by hydrogen bonding they are able to active a substrate or to increase enantioselectivity; this has been observed in Michael, Mannich and Henri reactions.[8,97] The high basicity of guanidines can be demonstrated by resonance theory, their protonation gives a cation which owns three equivalent resonance forms. This increases the stability and gives a better distribution of the positive charge and hydrogen-bonds system. This phenomenon is called: Y-aromaticity and occurs on the most basic function of the molecule, which is the imine (Figure 21).[8,98]

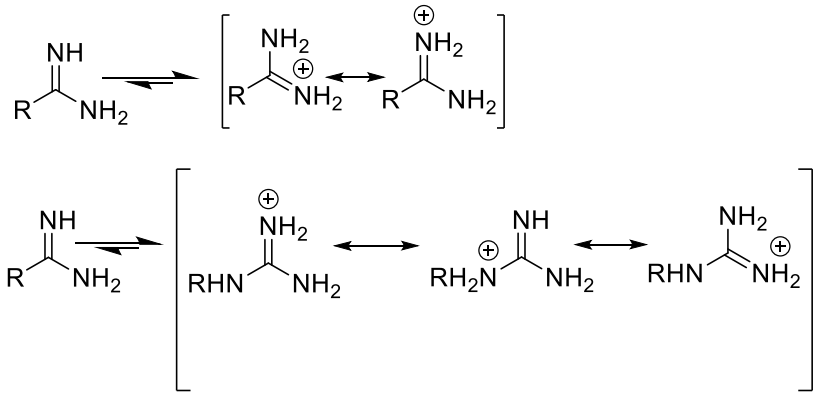


Figure 21. Different isomers of guanidine

The rigid structure of bicyclic guanidine makes the physical, chemical and even electronical properties different from their acyclic analogues. Bicyclic guanidines can also delocalise a positive or a negative charge between the three nitrogen and the structure stays planar due to the cyclic structure. Which is not the case for acyclic guanidines where the steric effect has a big role often leading to an orthogonal structure (Figure 22).[99] In an acyclic guanidine, when a nitrogen is substituted, different isomers of the C=N bond can be observed; but for cyclic guanidine only the conformation E_{anti} can be obtained. [99]

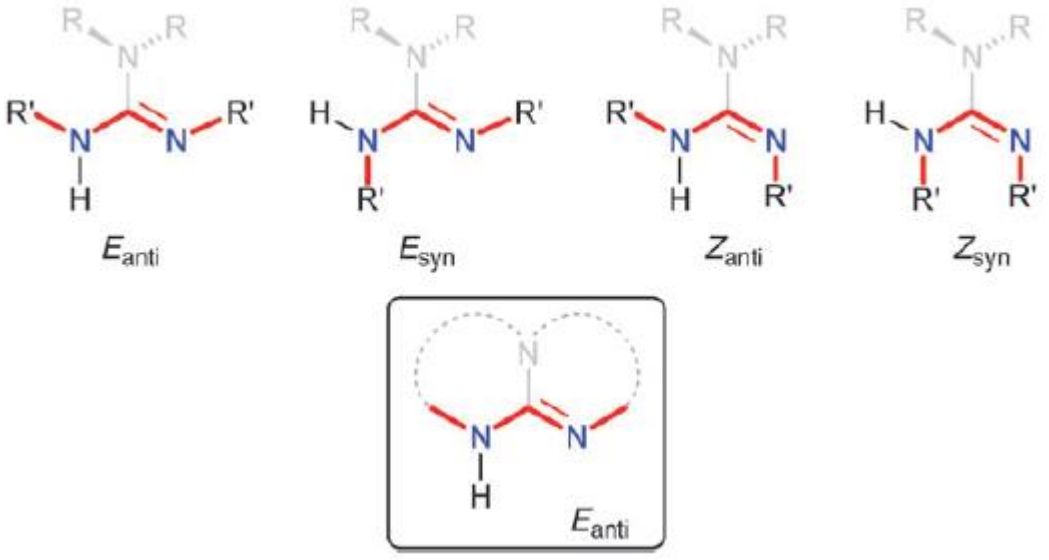


Figure 22. Different spatial conformation of the guanidine function in a molecule.[99]

4.3. Synthesis of guanidines

4.3.1. Acyclic guanidines

4.3.1.1. Thiourea derivatives

The first apparition of acyclic guanidine came in 1972 with a paper from Kishi where he used dithiocarbonimidate on a primary amine at 150°C to protect it from oxidation and resulted in a guanidine function.[100] Later many studies gave different pathways to introduce this type of function in a molecule, it involves a primary amine and an activated guanidine precursor, after a deprotection step, a free guanidine is obtained (Figure 23).[101]

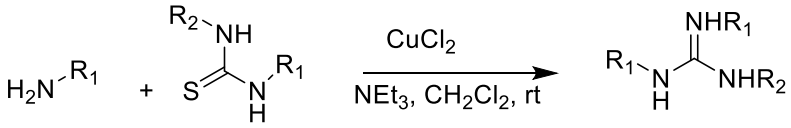


Figure 23. Synthesis of guanidine using thiourea as a starting material

As the yield reported was too low, in 1993 Kyoung investigated another route using thiourea derivates in presence of mercury or copper chloride as a desulphurising agent. Later it was replaced by mercury oxide because of their instability and their limitations to form certain compounds such as diglycosylgunaidines.[102,103]

4.3.1.2. Coupling reagent

In 2002, Manimala published a new method using EDCl (Figure 24) as a coupling agent to have a better desulphurisation than with mercury compounds. This leads to a higher yield, less side product and a straightforward way of purifying the guanidine by using chromatography. All the amines tried were aliphatic and gave a similar yield, they conclude that the ethyl carbamate protecting group introduced by EDCl is a good reagent for coupling primary and aryl amine. Instead of using HBr or NaOH that are known to cleave the de-protected NH_2 function, Me_3SiBr under reflux in DMF is the most favourable way to remove only the protective group.[101,104]

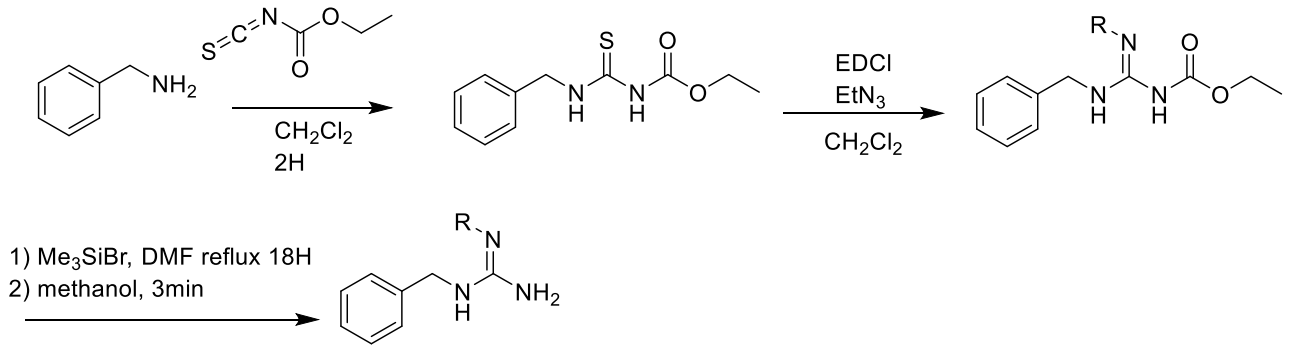


Figure 24. Synthesis of guanidine using EDCl as a coupling agent.

4.3.1.3. Urea derivatives

Urea is an oxygen analogue of guanidine despite this; it has been less investigated than thiourea or its sulphur analogue because of its stability (Figure 25). Bramm has highlighted this phenomenon in 1979, he investigated a new anti-flammable agent using urea derivatives. The synthesis of crude carbodiimine intermediate is high (around 83%) which reacts with different amines in different solvents, this leads to a large range of yield starting from 14% to 76%.[101,105]

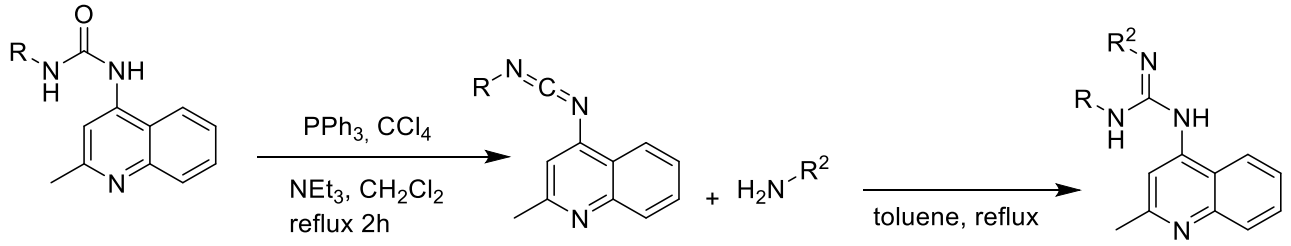


Figure 25. Synthesis of guanidine using urea derivative as a starting material.

4.3.1.4. N,N',N''-Trisubstitued guanidine

One of the most employed technique to synthetize guanidine was to treat amine with an electrophile amidine. In 1998, Goodman and co-authors published an alternative to thiourea derivatives by using guanidine hydrochloride as a starting material (Figure 26). The principle was to protect the two primary amines and transform the imine into a leaving group. This is followed by a nucleophilic attack and formation of the guanidine function.[101,106]

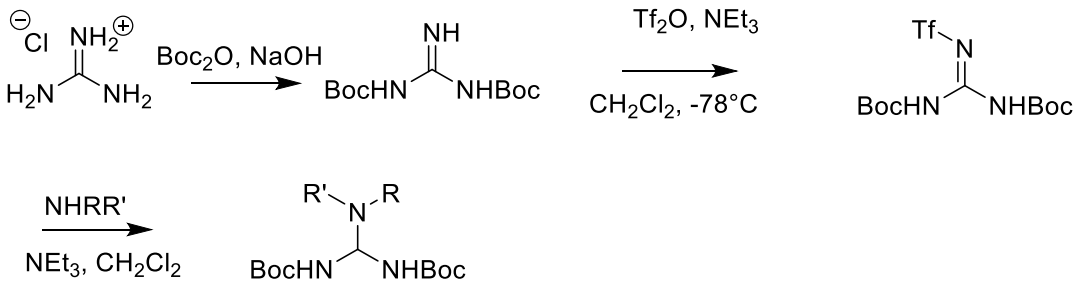


Figure 26. Synthesis of guanidine using guanidine HCl as a starting material and a tertiary amine as nucleophile.

4.3.2. Cyclic guanidines

Cyclic guanidine are observable in many natural products and compounds in medicine. Because of their facile way of synthesis they received a lot of attention in organic chemistry.[107]

4.3.2.1. Five membered ring

The easiest way to synthetize fiver membered ring guanidine is to use a cyclic derivative of thiourea. In this case the two secondary amine functions have to be protected and $HgCl_2$ is used as a Lewis acid to allow the formation of the guanidine function (Figure 27). Once the function built, the protection can be removed using an acid such as trifluoroacetic acid.[108] The oxygen analogue of the starting material can be employed as the intermediate formed during the reaction cannot be isolated and react immediately with amine to form the wanted product (Figure 28). One inconvenient of this method is the use of dimethyl chlorophosphate as a chlorinating agent, which is highly toxic especially through dermal absorption.[109]

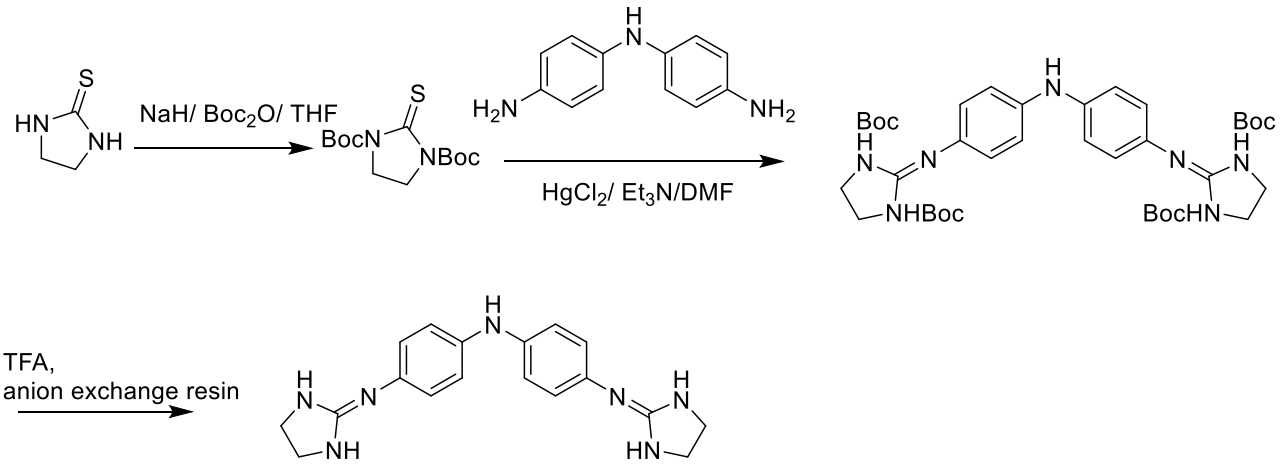


Figure 27. Synthesis of cyclic guanidine using a sulphur analogue as a starting material.

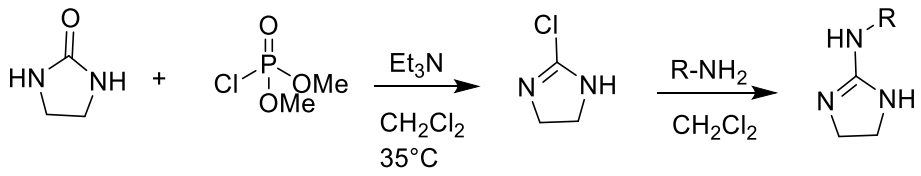


Figure 28. Synthesis of cyclic guanidine involving dimethyl chlorophosphate to chlorinate the starting material.

In organic chemistry 2-Chloro-1,3-dimethylimidazolium chloride is used as a strong dehydration agent or as a chlorinated agent for primary and secondary alcohol. 2-Chloro-1,3-dimethylimidazolium chloride reacts with amine to give the wanted guanidine by enhancing the cyclisation step: a spontaneous nucleophilic attack from the amine to the carbon attached to the chloride. This can be applied to form mono- and bicyclic guanidine (Figure 29).

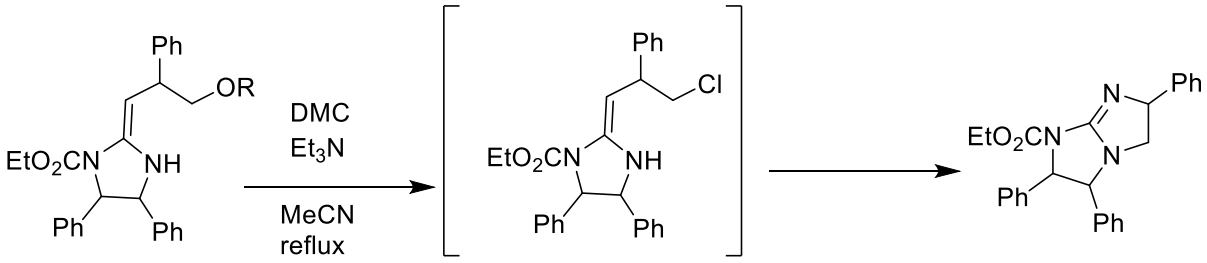


Figure 29. Synthesis of cyclic guanidine involving DMC to chlorinate the starting material.

4.3.2.2. Six membered ring

This type of cycle has been less studied than five membered ring but attracts chemists by its potential biological application.[101] The two most employed way to obtain a bicyclic guanidine is to introduce the guanidine function in the middle of the molecule by doing a double cyclisation using a triamine precursor and a cyclising agent. Alternatively, it is possible to do an intramolecular cyclisation of an alkylated monocyclic guanidine (Figure 30).[110] The first synthesis used to form bicyclic guanidine starting from monocyclic guanidine derivative was described by McKay, in this case the cyclisation is based on nucleophilic substitution followed by nucleophilic attack to form the ring. This synthesis route can be applied for bicyclic guanidine made of [5+5], [6+5], [6+6], [5+7] membered ring.[111]

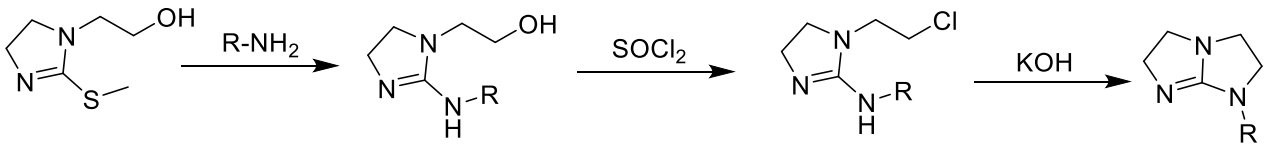


Figure 30. Formation of [5+5] bicyclic guanidine.

An alternative to monocyclic intermediate is the use of carboxylic acid derivates such as ethyl-ester-bases intermediate (Figure 31). This method was for the first time introduced by Ishikawa to prepare [5+7] and [7+5] bicyclic guanidine.[111]

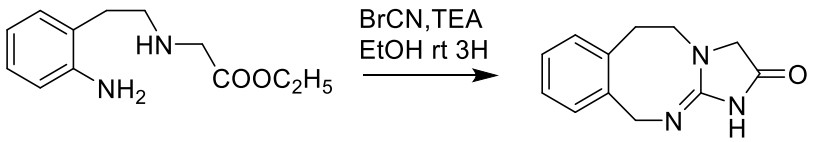


Figure 31. Formation of [8+5] bicyclic guanidine.

Another way has been investigated, instead of using monocyclic diamine as a starting material; it is possible to use a linear triamine (Figure 32). One of the first way to do is to use $CSCl_2$ as a cycling agent, the biggest inconvenient is the formation of toxic compounds such as thiosphogene or mecarptane.[112]

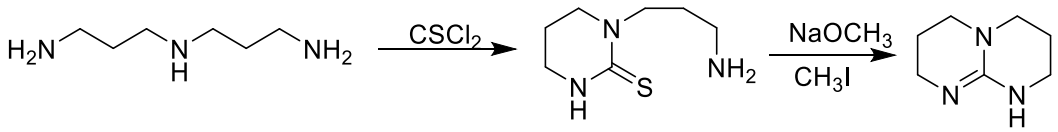


Figure 32. Formation of [6+6] bicyclic guanidine using $CSCl_2$ to cyclise the triamine.

Another way is to replace $CSCl_2$ by CS_2 but hydrogen sulphide is released and this is toxic. Later two US patent demonstrated a new alternative using a dehydration agent as a cyclic agent at high temperature (Figure 33). The intermediate formed contains an oxygen atom instead of a sulphur, this limits the toxicity of the reaction.[113,114]

Figure 33. Formation of [6+6] bicyclic guanidine using DMC to cyclise the first 6-membered ring followed by dehydration to form the second.

The most recent way to obtain a bicyclic guanidine using a triamine precursor is the one using guanidine salt as a cycling agent. Ammonia is released during the reaction but the gas can be trapped in water and neutralised later (Figure 34). This reaction leads to a salt and not a free base, to obtain it, the salt has to be treated with NaOH or KOH and then extracted.[112]

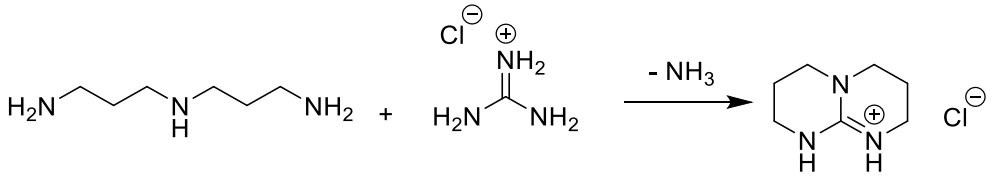


Figure 34. Formation of [6+6] bicyclic guanidine using guanidine.

4.4. Applications of superbases

4.4.1. Uses of superbases in organic chemistry

There is a lot of report about the use of superbase in organic chemistry, for example TMG or TBD can be used in elimination or Witting reaction as a basic catalyst or amidine as DBU can be used as a nucleophile. Superbase have also been used in Michael reaction involving nitrile or nitro groups in Strecker reaction, and even in transesterification reactions. [101,115]

4.4.1.1. TBD used in Ring opening polymerisation

TBD demonstrated capacities to catalyse the ring opening polymerisation (ROP) of cyclic esters. Waymounth demonstrated its high catalytic capacities and compared them to amidine compounds. In ROP, TBD acts like a nucleophile and forms an active intermediate able to react with other functions such as alcohol (Figure 35).[115]

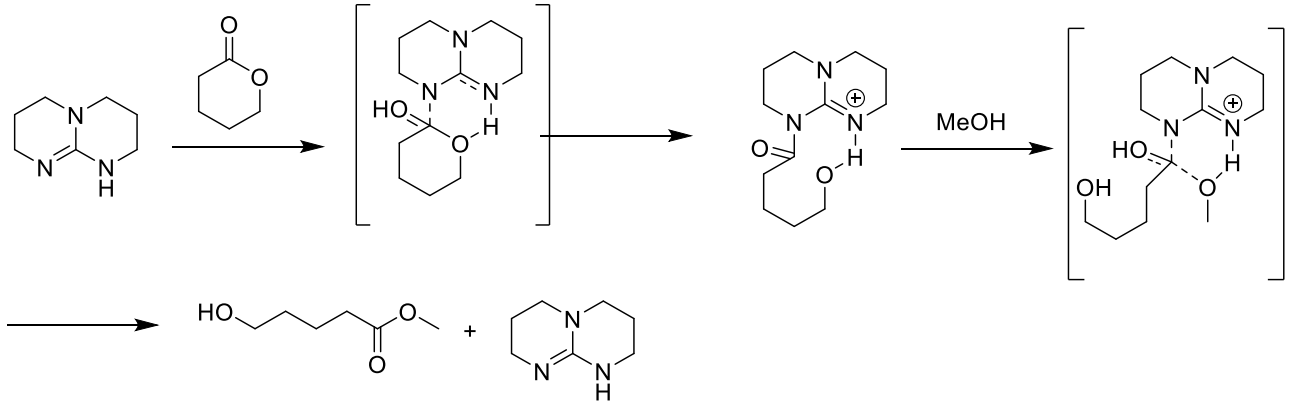


Figure 35. TBD acting as a catalyst in ROP.

4.4.1.2. Utilization of superbases in Witting reaction

TBD and its analogue MTBD are 100 times more basic than TMG and are able to catalyse the addition of a nucleophile to an unsaturated system. Because of this, they can be useful in Witting reaction. They can replace organolithium compounds normally used as a base catalyst or other ionic strong base, which can react with other functional group such as carboxylic, or ester function contain in the phosphorane starting material (Figure 36). Also normal strong organobase are highly sensitive to air and moisture so the reaction needs to be conducted under inert atmosphere which is not required while using superbase.[116]

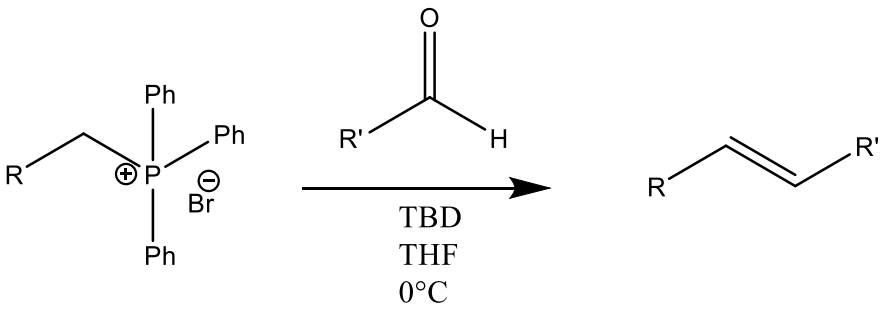


Figure 36. Application of TBD in Witting reaction.

4.4.1.3. Similar: Superbases in Henry (nitro aldol) reaction

Henry reaction is the most well-known carbon-carbon forming reaction. Many efforts have been made to find an asymmetric version of the synthesis. Guanidines interact with nitro compound and form the nitronate anion using electrostatic interactions but also hydrogen bonds (Figure 37). Because of this intermediate structure, the anion formed is in a chiral environment; this leads to a control of the product stereochemistry and increases the enantioselectivity of the reaction (Figure 38).

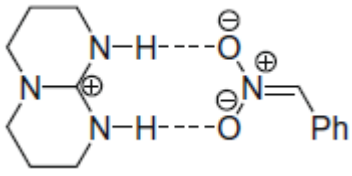


Figure 37. Hydrogen bond system built between TBD and a nitro-compound.

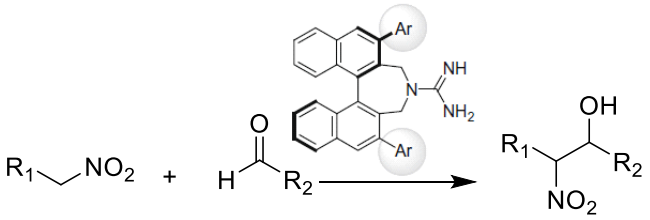


Figure 38. Application of guanidine derivative in Henry reaction.

4.4.2. New era: Superbases as green chemicals:

4.4.2.1. CO_2 capture

Emission of CO_2 is a major problem for climate changes and receive a high attention from all around the world. The most well-known way to capture CO_2 is to use an aqueous ammonia solution, this is cheap, highly reactive and effective. But this method has inconvenient, it is corrosive hard to recycle and a lot of solvent is lost during the process. Later the idea of using ILs for their physico-chemical properties came in mind. Jessop and Weis described a way to catch CO_2 using DBU as a proton acceptor and alcohol as a proton donor.[117] This demonstrated high reactivity and capacity to catch CO_2 also requires less energy than aqueous ammonia to desorbe CO_2. One of the biggest problem with ammonia was its volatility, same for alcohol. To solve this problem, Congmin Wang and co-authors replaced alcohol by imidazolium-based ILs and ammonia by superbase to obtain a non-volatile mixture (Figure 39).[117]

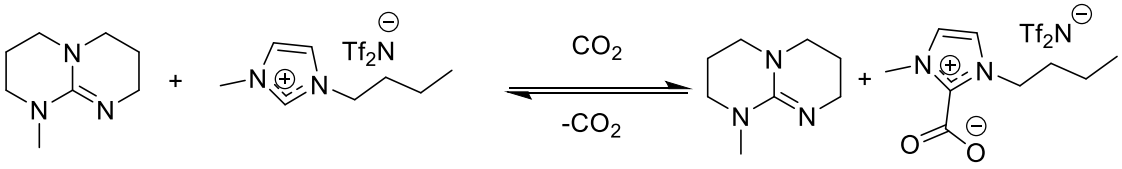


Figure 39. CO_2 capture by a mixture of m-TBD and imidazolium-based ILs.

4.4.2.2. Superbase salts for cellulose dissolution: protic ionic liquids

Because of their high basicity and high capacity to attract hydrogen they can form salt with weak acid such as propionic, formic or acetic acid.[9] TMG is the most used acyclic guanidine to form salt. ILs-based on guanidine are known to be chemically and thermally stable, this comes from the high

proton delocalisation between the three nitrogen atoms. Also in 2011 A.King and co-authors discovered that ILs based on TMG and formic or acetic acid are able to dissolve rapidly cellulose and are distillable so recyclable with a purity of 99%.[118] This distillable capacity can be explained by the high acidity of the [TMGH] cation allowing the dissociation of the acid base salt leading to two neutral and volatile species (Figure 40).[118]

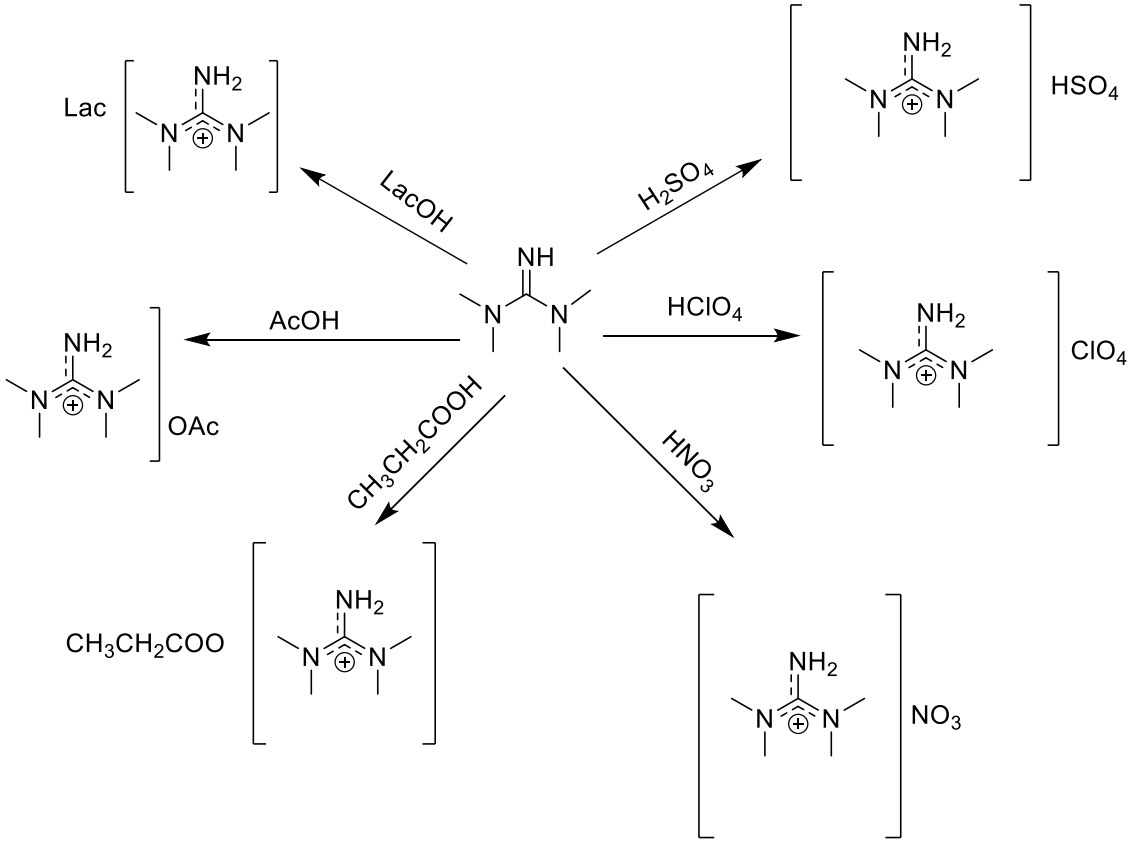


Figure 40. Some examples to obtain various TMG-based ILs.

Even if they are able to dissolve cellulose, their characteristics related to their structure such as high melting point and high viscosity are a problem for lab experiments using a classic magnetic stirring. Also they are limited to 10 wt% cellulose dissolution.[79] A lot of superbase ILs such as immidazolium-based ILs were investigated for cellulose dissolution but they require temperature higher than 90°C enhancing cellulose degradation.[15] So bicyclic guanidine were investigated as a potential class of ILs. Because of their rigid bicyclic structure, they are less affected by steric effect than their acyclic analogue (Figure 41).[9]

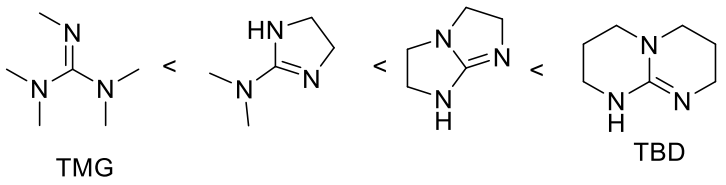


Figure 41. Classification of superbase according to their basicity, TMG has the lowest and TBD the highest basicity according to their Pka

The structure of the cation plays a role in cellulose dissolution, planar cation have better abilities than non-planar structure. Also the capacity of π-electron delocalisation of the positive charge in the bicyclic guanidine helps the dissolution, because of their aromatic system they build stronger H-bonds with cellulose than acyclic guanidine cation.[119] These characteristics explain why chemists started to be interested in bicyclic guanidine species in ILs such as TBD and its methylated version mTBD.

5. Introduction to the laboratory work

The laboratory works started with a previously phosphonium based ILs, synthetized by another student. The aim was to use it as a NMR solvent for cellulose without using a second classic NMR solvent such as DMSO. The issue was the overlapping signals from the IL and the cellulose. The work was focus on a way to make the IL ''disappear'' from the spectrum and only observe the cellulose signals.

Later the work continued with the investigation of existing superbase's structure. The goal was to find a way to modify them to obtain a new structure. TBD was the first choice, as its analogue m-TBD is commercially available; the alkylation process involved the ethyl, allyl, butyl and hexyl ramifications. The work started by trying to find a suitable procedure to obtain the wanted product and to optimise the synthesis until a decent yield and purity are reached.

Once these new structure synthetized, the goal was to create the corresponding ILs. Only the acetic acid was employed because acetate anion is the most environmentally friendly and is widely used in cellulose dissolution process. The ultimate goal for these ILs was to dissolve cellulose and if they do it, find out how much cellulose they can dissolve.

Later during the work, the aim was to synthetize new triamine precursor to create other structure of superbase that are not made of existing compound. For this, it was important to find cheap and green starting materials but also a straightforward procedure.

6. Aims of the study

The quantity of fossil supplies is decreasing and environmental degradation are a worldwide issue, one of the biggest challenge is to find alternatives to these materials. Cellulose is the most abundant biomaterial on earth and can find many applications such as textile industry. The limitations are the solubilisation and analysis of cellulose. Even if a lot of effort have been done to find a proper solvent to it, most of them are still toxic, corrosive, non-reusable so potentially hazardous for the environment. The aim of this work was to design and synthetize new solvents for cellulose which would be green enough to not give dangerous side product while degradation or once release in nature, high capacity of dissolution, if possible distillable for reuse and finally easy and cheap to synthetize. Thermal stability and structure were investigated using TGA and NMR respectively.

7. Experimentals and Results.

In this section, each reaction done in the laboratory will be explained by the given procedure and results will be analysed right after it. In a first part, two different works are presented: kinetic studies on one IL synthetized previously, tested on cellulose and based on phosphonium structure. As it dissolves cellulose in a satisfying way, the purpose is to optimise it and use it as a NMR solvent for cellulose. In addition, synthesis of a new ILs based also on phosphonium derivatives. In a second part, the work will be focus on the synthesis of new ILs based on superbase structure. In this section three topics are described: synthesis of ILs based on TBD and tests their cellulose dissolution capacities, then synthesis of new triamine precursors for superbases and finally alkylation of TBD derivatives followed by synthesis of ILs based on them and cellulose dissolution capacities tests.

Kinetic studies of tetrabutyl phosphonium acetate:

This IL has been previously prepared in our laboratory and tested on cellulose dissolution. One issue of cellulose analysis is its signals; they overlap with many other signals from IL or organic solvents; this resulting in a non-clear spectrum. One way to solve this problem is to make the IL ''disappear'' from the spectrum, it means that the hydrogen from the molecule are not visible. To do this it is possible to do a proton exchange using deuteration process. This process consists in replacing hydrogen atoms in a molecule by deuterium atoms that are not visible on a classic proton NMR spectrum.

Before doing the kinetic studies the deuteration has been tested: in two ADV of 23ml respectively charged with 1g of IL, 1ml and 5ml of fresh D_2O were added to obtain two IL:D_2O ratio of 1:1 and 1:5 volume equivalents. During three days, they were heated to 160°C then the D_2O was evaporated under high vacuum then replaced by same amount of fresh D2O and a new deuteration cycle was run. This experiment was run during 5 cycles. At the end of this only the proton in alpha position and the proton from acetic acid have been deuterated, the rest of protons are not acidic enough to undergo the same exchange. The result of the deuteration is satisfying enough and the kinetic studies can start.

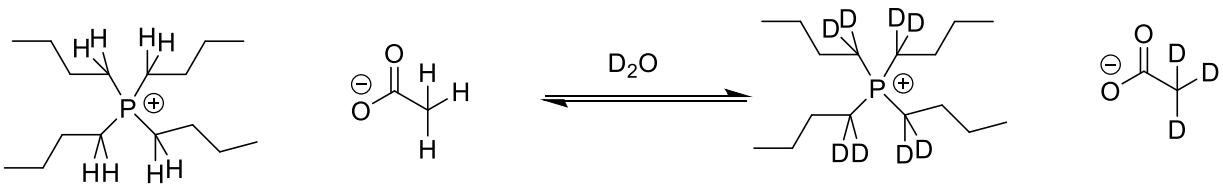
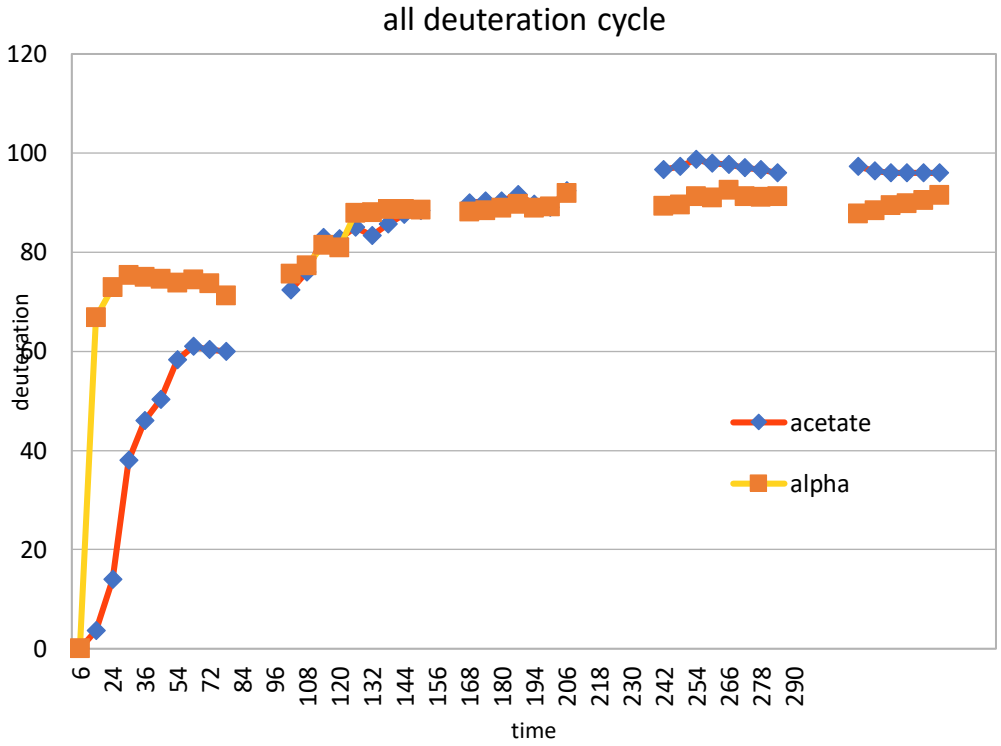


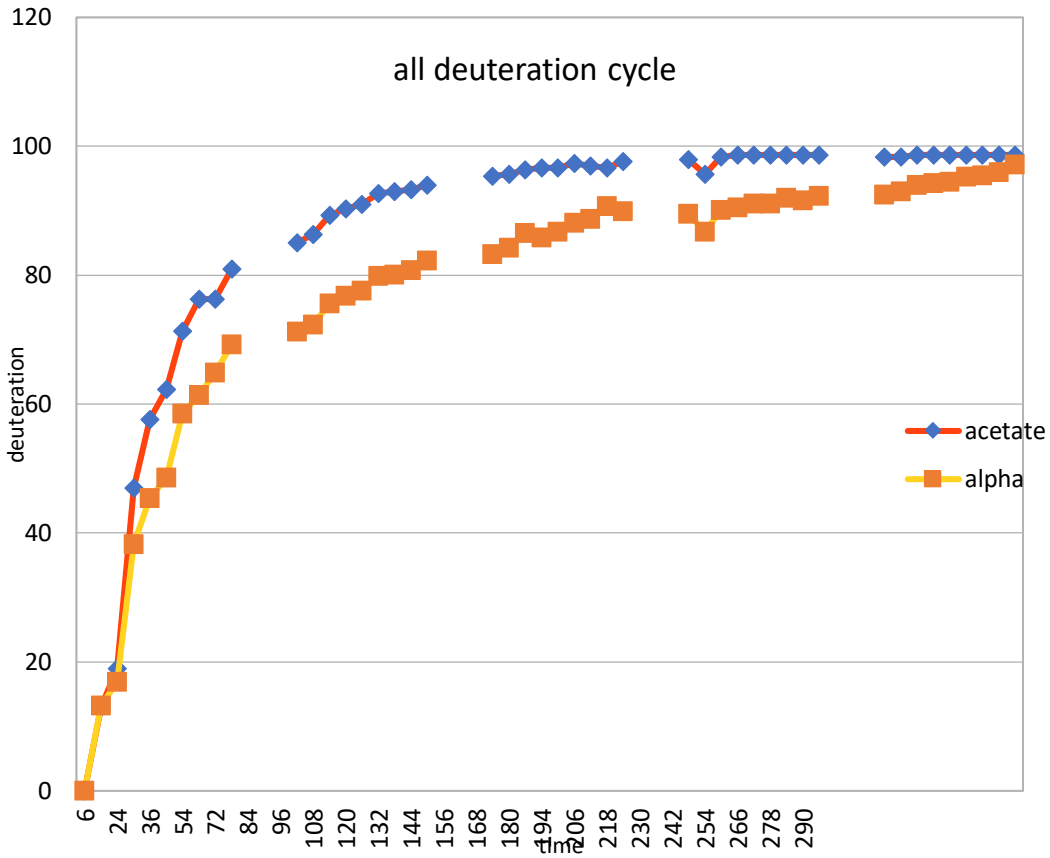
Figure 42. Deuteration of [P_{4444}] [OAc]

The kinetics are followed by NMR using the value of the integrals of each peak, a curve of deteuration evolution can be built:



Graph 1. Representation of deuteration of [P_{4444}] [OAc] (1:1 (w:v)) at 160°C each 8h

This curve is not perfectly regular, at some points,it means that the deuteration is not evolving or even the reverse reaction is observable (Graph 1). This proton exchange is an equilibrium so a reversible reaction, this explain the shape of the curve, but the deuteration process is a favourable reaction so at the end the product will be deuterated. The ration 1:5 gives a higher percentage of deuteration and a more regular shape of curve (Graph 2).This is explain by the bigger amount of D_2O even if the deuteration is slower at the beginning of the process, the amount of deuterium is more important so the equilibrium will be shift to the deuterated compound. So to obtain a deuterated IL suitable for NMR analysis of cellulose, the most efficient ration will be the 1:5 IL:D_2O.



Graph 2. Representation of deuteration of [P_{4444}] [OAc] (1:5 (w:v)) at 160°C each 8h

Procedure:

In two different ADV respectively charged with 1g of [P_{4444}][OAc] 1ml and 5ml of D_2O were added to obtain a ration of IL:D2O of 1:1 w/v and 1:5 w/v. The mixture was stirred at 166°C, every 6h the mixture was cooled down, 0,6ml of the liquid was used for collecting NMR data and put back in the reactor. After 72H, the solvent was dried and fresh D_2O was added in the same ration as before, a new cycle was started. This was repeated for 5 cycles. At the end the signal from proton in alpha position and from the acetic acid were not visible anymore.

Synthesis of (3,3,3-Fluoropropan-1-yl) trimethylphosphonium iodide

As the deuteration exchange occurs only on the alpha proton and the acetate in the [P_{4444}] [OAc], the aim of this synthesis was to find an alternative where all the proton would be acidic enough to undergo the deuteration, the cellulose dissolution capacities of the following compounds were tested in our laboratory and satisfying enough to try the deuteration exchange. The experiment was run in an ADV at 160°C so the IL needs to be thermally stable.

After TGA analysis, the compounds show thermal decomposition at 391.44°C. The phosphonium atom makes the proton form the three-methyl group and the two from the alpha position acidic enough to be exchanged also, the three atoms of fluorine acidify the proton in beta position. (Figure 43)

Concerning the NMR spectra of [$P_{1113}F_3$] [I] and [$P_{1113}F_3$] [OAc] In theory the three methyl groups attached to the phosphonium should be a singlet, but it appears to be a doublet, this can be explained by the free rotation of the P-CH2 bond and the electronics interactions between the phosphonium atom and the fluorine. In addition, the two CH2 groups on the chain should give two different triplets with a different chemical shift but the spectrum shows a multiplet where it is hard to define which peaks belong to which CH2 group. This is due to the three-fluorine interacting with the proton and change peak's aspect. The metathesis from the iodide to the acetate gives a yield of 99.6%, after TGA analysis the vapour pressure is at 202°C this makes the [$P_{1113}F_3$] [OAc] stable enough for deuteration experiment.

This reaction has to be run under reduced atmosphere to this; the easier way is to use the glovebox where the oxygen pressure is lower than 0,5ppm same for the level of water. These conditions were employed because trimethylphosphine is pyrophoric and reacts spontaneously if exposed to air. In a large quantity it can even self-heating and catch fire so working in a normal fume hood is not appropriate. Also once the reaction done, the ADV has to be opened carefully because of the pressure and the eventually unreacted trimethylphosphine.

Procedure:

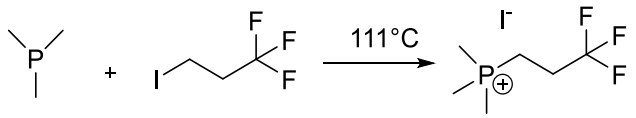


Figure 43. Synthesis of (3,3,3-Fluoropropan-1-yl) trimethylphosphonium iodide

To a 125 ml Acid Digestion Vessel (ADV), equipped with a stirrer bar, 66,6 ml (66,638 mmoles, 1 Eq,) of trimethylphosphine (1M in Toluene) and 8,3 ml (73,302 mmoles, 1,1 Eq,) of 1-Iodo-3,3,3-Trifluoropropane were added under inert atmosphere. The ADV was tightly closed and the reaction mixture was stirred overnight at 111°C. Next day a wet white solid was observed. The solid was washed with fresh HPLC Toluene and dried at reduce pressure. Yield: 90%

Cellulose dissolution is based on inter and intramolecular hydrogen bonds, they are formed between the proton from hydroxyl group and the anion from the ILs.[120] So, the dissolution depends in a big part on anion's basicity.[17]

One inconvenient from halides anions is their toxicity but are also corrosive for the equipment used, this make them aggressive for the environment.[17] ILs based on carboxylic anion showed to be able to decrease the melting point and the viscosity and increase the hydrogen bonding system.[121] This exchange of anion can be done by metathesis using silver acetate, one important parameter with this reaction is the light (Figure 44). The reaction if possible has to set up and run in the darkest environment possible because of the silver particles. With contact of light, they take a dark colour hardly removable, so this is important to cover the flash with aluminium foil to prevent this. The filtration should also be done in the dark and if the reaction was covered properly, the filtrate is lightly yellow. To be sure to remove all the silver particles another filtration is done using siring filter size 0,2µm three times.

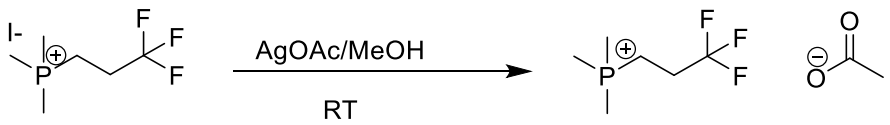


Figure 44. Synthesis of (3,3,3-Fluoropropan-1-yl) trimethylphosphonium acetate

Procedure:

To a 100ml RBF 4g of (3,3,3-Fuoropropan-1-yl) trimethylphosphonium iodide, 60ml of methanol and 0.98 equivalent of silver acetate were added and stirred at room temperature during 24h under light protection. Then the reaction was filtrated through Celite 545 and a funnel size 4, solvent was removed by a rotavapor. More solvent was added to filter again the product with syringe filters to avoid silver particles, methanol was dried a second time and the product dried with a high vacuum rotavapor. Yield: 95%

In a concern of environmental friendly compounds, a new class of ILs easier to recycle, more polar, with a lower viscosity and melting point has been studied: Superbases ILs.[9] They belong to a specific group with strong basicity and a high capacity of biding hydrogen. In particular, guanidines forms easily salt with weak protic acid such as AA or propionic acid, thus ILs are easily synthetized. Protic ILs based on ganidines are thermally and chemically stable, this can come from the cation that they

form which owns a high-delocalised charge.[9] The second part of this work is focus on cyclic guanidines and more specifically: TBD and its derivatives.

Synthesis of TBD derivatives.

The first superbases studied to form new ILs were TMG and DBN, they offer new recycling methods using distillation.[122] Derivatives from guanidines such as TMG or DBN gave the most important cation precursors for new superbase ILs, especially TBD and its derivative m-TBD.[9]

TBD has been the first superbase studied in this work because it was commercially available and only one of its analogue has been studied, the aim was to find out if others would be interesting for cellulose dissolution.

The synthesis of A-TBD, b-TBD and h-TBD were based on the same procedure, only the alkylating agent changed, the TBD used for the alkylation has been synthetized in our laboratory even if they are commercially available because of their high cost. The NMR analysis were run in d6-DMSO.

Before any alkylation, some impurities from TBD synthesis were present; they can come from the propanediamine or cyclisation agent, so it needed to be purified (Figure 45):

Procedure:

In a RBF of 500ml, 20g of non-pure TBD (0,9 mol, 1 equivalent) were charged and dissolved in 100ml of toluene, the solution was heated at 60°C until obtaining a clear solution. 130ml of heptane were added to precipitate the product, then stored at -20°C overnight. After filtration, the solvent was removed under vacuum. White crystals were obtained. Yield= 97%

Once the purification done, and dried overnight using a Schlenk line, alkylation process can begin.

General Synthesis:

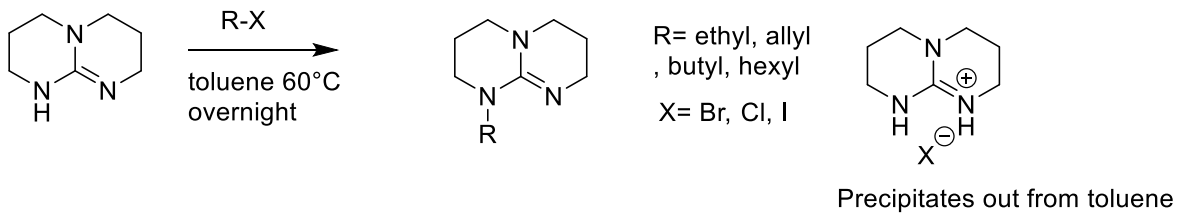


Figure 45. Global synthesis of alkylated TBD

Into a two necked 100 ml round bottomed flask 20 g (89.54 mmoles, 1 Equivalents) of TBD were charged and dissolved in 100 ml of Toluene. 9.49 g (44.7 mmoles, 0.5 Equivalents) of Hexyliodide were added dropwise under reflux. The reaction mixture was kept at 60°C under vigorous stirring overnight. Then the crude product was filtered. Finally, the solvent was removed under vacuum. Yellow viscous oil was obtained, yield= 50%.

In these reactions the formation of the salt from TBD is unavoidable, the challenge is to separate it from the wanted product, as this one is non-polar it will be well soluble in a non-polar solvent such as toluene counter to the salt which will precipitate. Thus, the product can be separated by filtration or decantation. The formation of the salt was also a problem for the yield, as the free halide reacts with TBD there is competition between the alkylating agent and it, this leads to lower yield. This could be solved by increasing the amount of TBD, in this case the alkylating agent is able to react fully, this leads to a yield of 50%. Even if the yield could be higher this is not a problem as the salt can be deprotonated in water using NaOH, after this the TBD can be extracted using dichloromethane and used again for another alkylation process.

Synthesis of h-TBD.

Before using this general synthesis route, further synthesis have been tried. First the HexylBromide was tried in a ratio of TBD: HexylBromide 1:1,17 in cyclohexane during four hours at room temperature, after washing it with ethyl acetate, the NMR spectra shows only signals from starting material. This leads to the conclusion that the conditions of the reaction themselves were not the good one such as bromide is a good leaving group. To be sure of this, the alkylation is tried again using in parallel HexylIodide in a ration TBD: HexylIodide 1:0,5 in toluene same using HexylBromide, the addition of the alkylating agent is made at 120°C, then the reaction is kept at 60°C overnight (Figure 46). The day after the NMR spectra shows for the HexylIodide three products: TBD, mono-alkylated TBD but the major product is a double-alkylated TBD. About the HexylBromide the NMR shows the same but with a mono-alkylated TBD as the major product. The conclusion of this is that the HexylIodide is too reactive to stop at only one alkylation and the Bromide is the best choice (Figure 47).

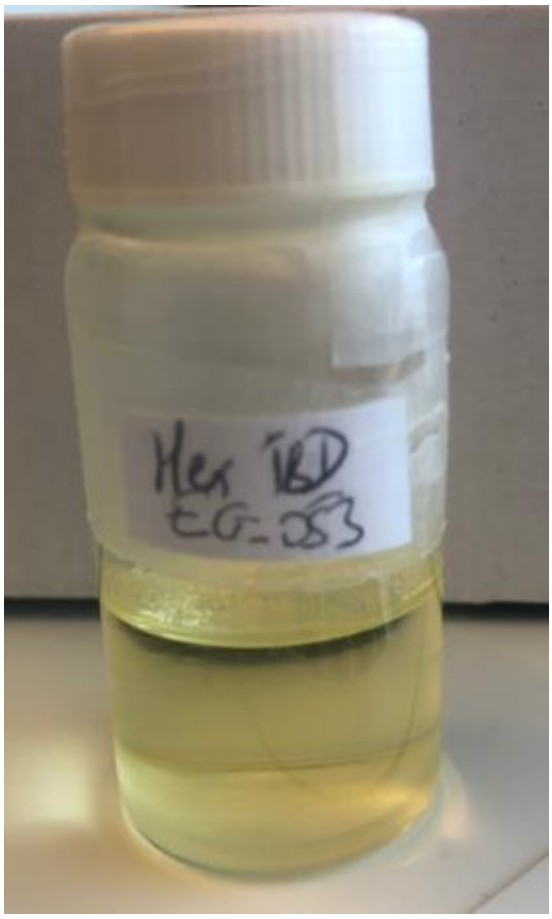


Figure 46. Picture of h-TBD obtained from TBD and HexylBr

Synthesis of e-TBD.

This experience has been repeated to alkylate TBD using ButylBromide and ButylIodide, the conclusion is the same, ButylBromide is the best choice.

Synthesis of AllylTBD

Two reactants have been used: AllylChloride and AllylBromide in respectively acetonitrile and toluene. The reaction with the AllylBromide gave the best yield.

Synthesis of e-TBD and m-TBD.

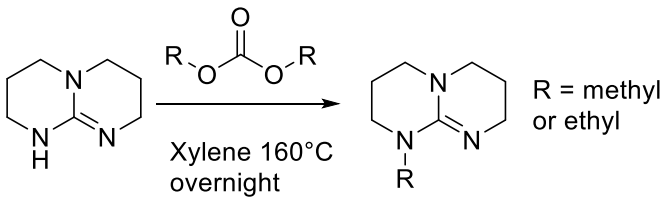


Figure 47. Synthesis of m-TBD or e-TBD

General procedure:

Into a two necked 100 ml round bottomed flask 20 g (89.54 mmoles, 1 Equivalents) of TBD were charged and dissolved in 51 g (268.62 mmoles, 3 Equivalents) of diethylcarbonate were added dropwise under reflux. The reaction mixture was kept at reflux under vigorous stirring for 24 h. Then the crude product was filtered. Finally, the solvent was removed under vacuum. Yellow viscous oil was obtained, yield= 50%,

DEC and DMC are used as alkylating agent because they are less toxic than EthylBromide or MethylIodide for instance. In this case we use the alkylating agent as a same excess because with heating they tend to form ethanol and methanol respectively and become less reactive, so the yield decreases. This kind of reaction needs high temperature to be efficient so it requires a solvent with a high boiling point, Xylene is convenient because it can be evaporated using a rotavapour (Figure 47).

Purification of alkylated TBD.

All the synthesis of TBD derivatives give a non-pure product containing: unreacted, mono and double alkylated TBD and need to be purified. Three methods have been processed, one is a liquid-liquid extraction and two are distillation. Before any purification, a colourless oil can be observed and after some time a white solid appears. The NMR reveals that this is unreacted TBD, the alkylated version can solubilize around 15% of TBD, after this it will precipitate out from the oil.

Even if toluene is a non-polar solvent, some [TBDH][X] is partially soluble in it, a way to remove this salt from it is to first dry the solvent and obtain an oil/solid mixture, solubilise it in a polar solvent and deprotonate the TBD salt with a base. Alkylated TBD is more soluble in non-polar solvent than polar, so a liquid-liquid extraction can be done. After drying the organic phase, a mixture of mono and double-alkylated TBD is visible by NMR, this can be further purified by distillation.

A second way to do is to process by classic distillation. Using a micro-distillation operator to avoid losses of product and an oil pump, which provides a vacuum about 10 mmbar. The first liquid to distil is the product of interest, the non-alkylated TBD cannot be distilled because it forms a salt as [TBDH][X-] and it is not volatile. Most of the impurities will not be distil either. The limit of this method is the boiling point of the compound at this pressure: ButylTBD can be distilled like this around 200°C but the AllylTBD need a higher temperature and the silicone oil used for this cannot reach higher temperature than 230°C.

Another way to purify the product is to use a Kugelrohr distillation, in this case the pressure is lower (around 0,5 mmbar), in this situation the b-TBD has a boiling point of 140°C, the h-TBD 180°C and the A-TBD 220°C. This method improves the yield of distillation this is also faster and easier to design in a laboratory. After this distillation a small amount of TBD is still visible on the NMR spectra (around 7-9%) but no more double-alkylated TBD.

After the distillation the amount of TBD is too low and is fully soluble in the mixture, to remove it, it is possible to make it precipate by complexation with CO_2 (Figure 48).

General procedure:

Into a 10ml RBF 0.5g of alkylated TBD (1 equivalent) were charged in 10ml of toluene and equimolar amount of CO_2 was added. The reaction mixture was stirred during half an hour, filtrated and the solvent removed. Once this last purification done, the amount of TBD was between 1 and 3%, this make the product pure enough for further reactions. At the end of theses synthesis all compounds obtained are viscous oil.

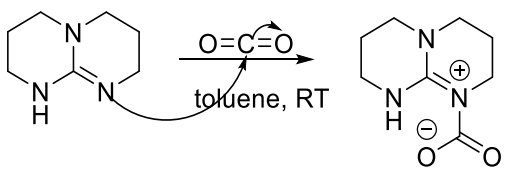


Figure 48. CO_2 capture by TBD

During alkylation a part of TBD reacts with the free halide released and forms a salt, this can be recycled by treatment with a strong base in a polar solvent and used again for alkylation (Figure 49).

General Procedure:

In a RBF of 100ml, 5g of [TBDH][X] were charged, equimolar amount of sodium methoxide in 50ml of methanol was added. The mixture was stirred for 15min, 25ml of dichloromethane were added to precipitate the inorganic salt formed, the purified TBD stayed in solution. Once the reaction filtered and the solvent removed, a white solid was obtained. For more purity, this can be distilled or recrystallized from toluene.

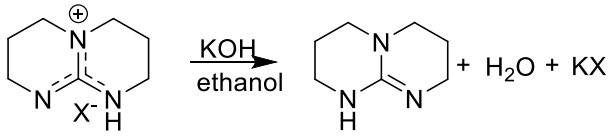


Figure 49. Neutralisation of the base as a salt and obtaining the product as a free base

General procedure:

1g of [TBDH][Br] (0,005 mol, 1equivalent) was charged in a RBF of 25 ml, 10 ml of a NaOH solution (0,4g 2equivalent) were added, then the mixture was stirred for half-an-hour. The aqueous phase was washed twice with cyclohexane, the organic phase was dried to give a white solid.

Synthesis of ILs based on alkylated TBD.

Once these compounds obtained in a large enough amount and with a satisfying purity, the synthesis of the ILs can begin. The counter anion used for this is the acetate anion from acetic acid. No matter the chain used in the alkylation process, all the ILs obtained are liquid at room temperature, the colour is from light yellow to dark-orange it depends on the hydrolysis due to air moisture contact during the reaction (Figure 50)

Procedure:

Into a 10ml RBF 5g of alkylated TBD were charged, equimolar amount of AA was added; the reaction mixture was stirred at room temperature during 1H. Yield 95%.

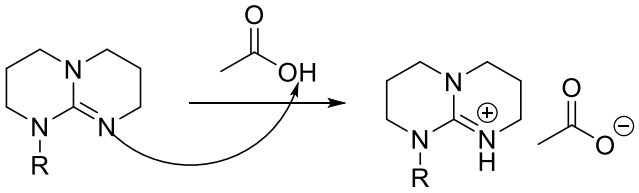


Figure 50. Base attack from TBD to acetic acid

The amount of AA is controlled by NMR, the integral value for it has to be three, this corresponds to the number of proton on the methyl group on the anion. NMR and TGA made characterization of ILs.

To test the cellulose dissolution capacities, each cellulose dope were placed into a 4ml vial and let stirred overnight at room temperature, then at 65°C to finish with 80°C. The evolution of the dissolution is followed by NMR spectra and microscope imaging using polarized light (Figure 51). The reaction cannot be heated up higher than 80°C because cellulose will start to decompose and becomes dark.

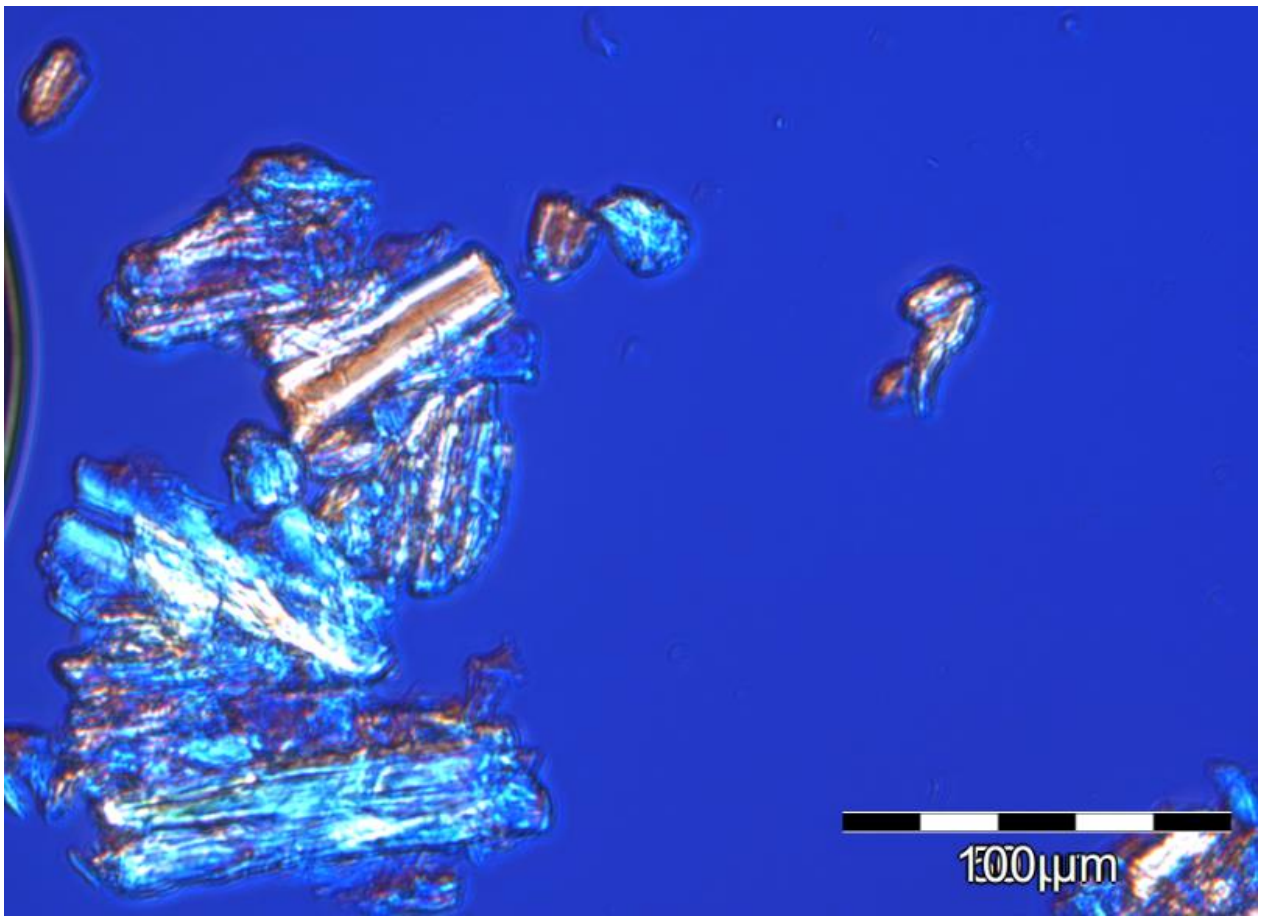


Figure 51. 2 wt% MCC non dissolved in DMSO. This picture is used as a reference for cellulose dissolution test.

e-TBD, A-TBD, and b-TBD don´t dissolve cellulose at all even at 80°C, they are also extremely viscous and don´t stir properly.

A-TBD after NMR analysis is not stable and forms enamine by activation from heating, at the end a light brown gel is obtained, this makes the IL not suitable for cellulose's studies (Figure 52).

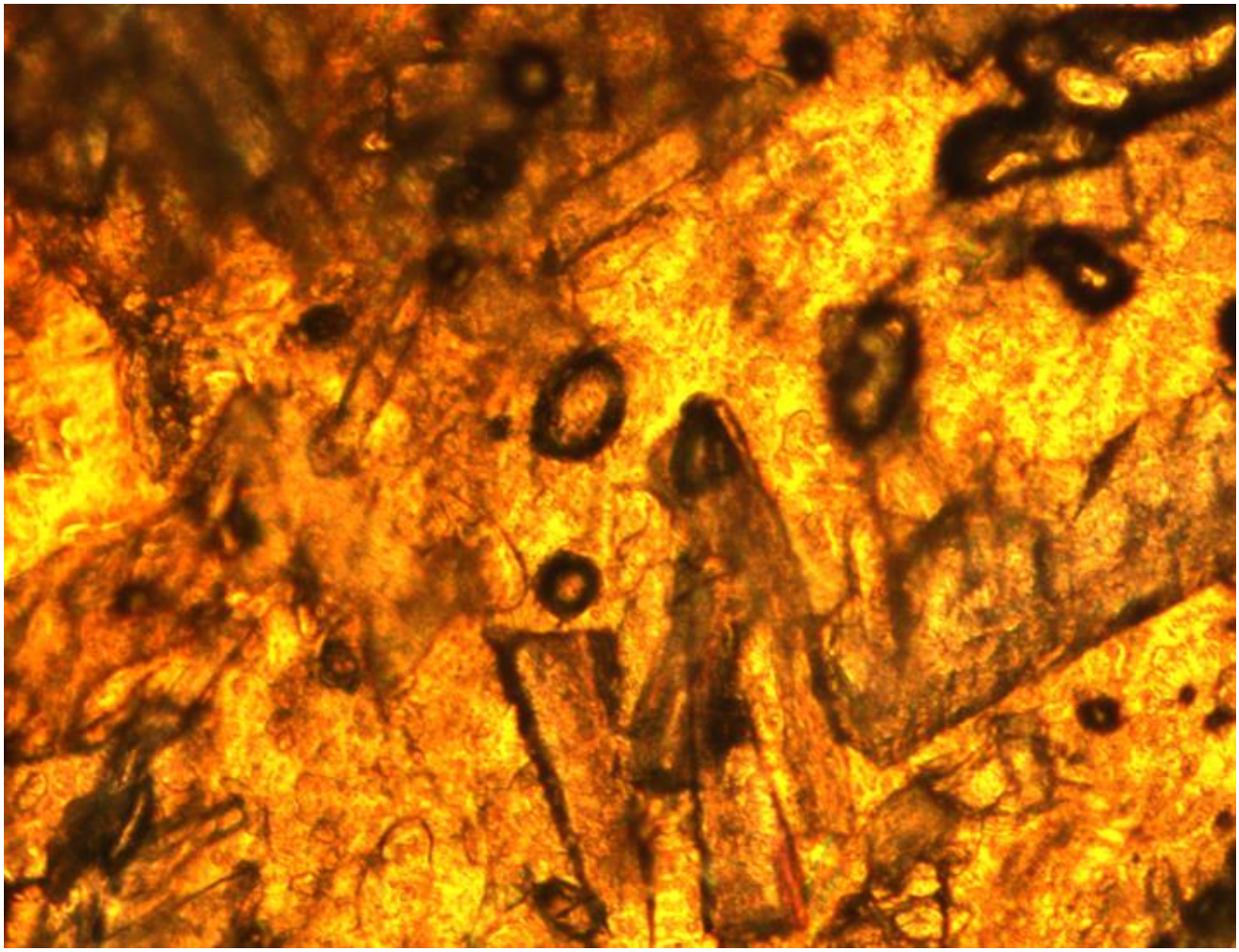


Figure 52. Picture of 5 wt% cellulose into [A-TBDH][OAc] after overnight reaction at 80°C, taken by an optical microscope using polarized light. The solution is not clear and crystals are observable.

h-TBD dissolves cellulose until 10 wt% at 60°C (Figure 53), it becomes a very viscous yellow oil. This has to be mixed with d6-DMSO to be analysed by NMR. The same experiment has been done at 80°C, the spectra shows a small peak of cellulose decomposition (around 2%) but the ionic liquid is stable.According to the TGA it has a thermal stability of 180°C.

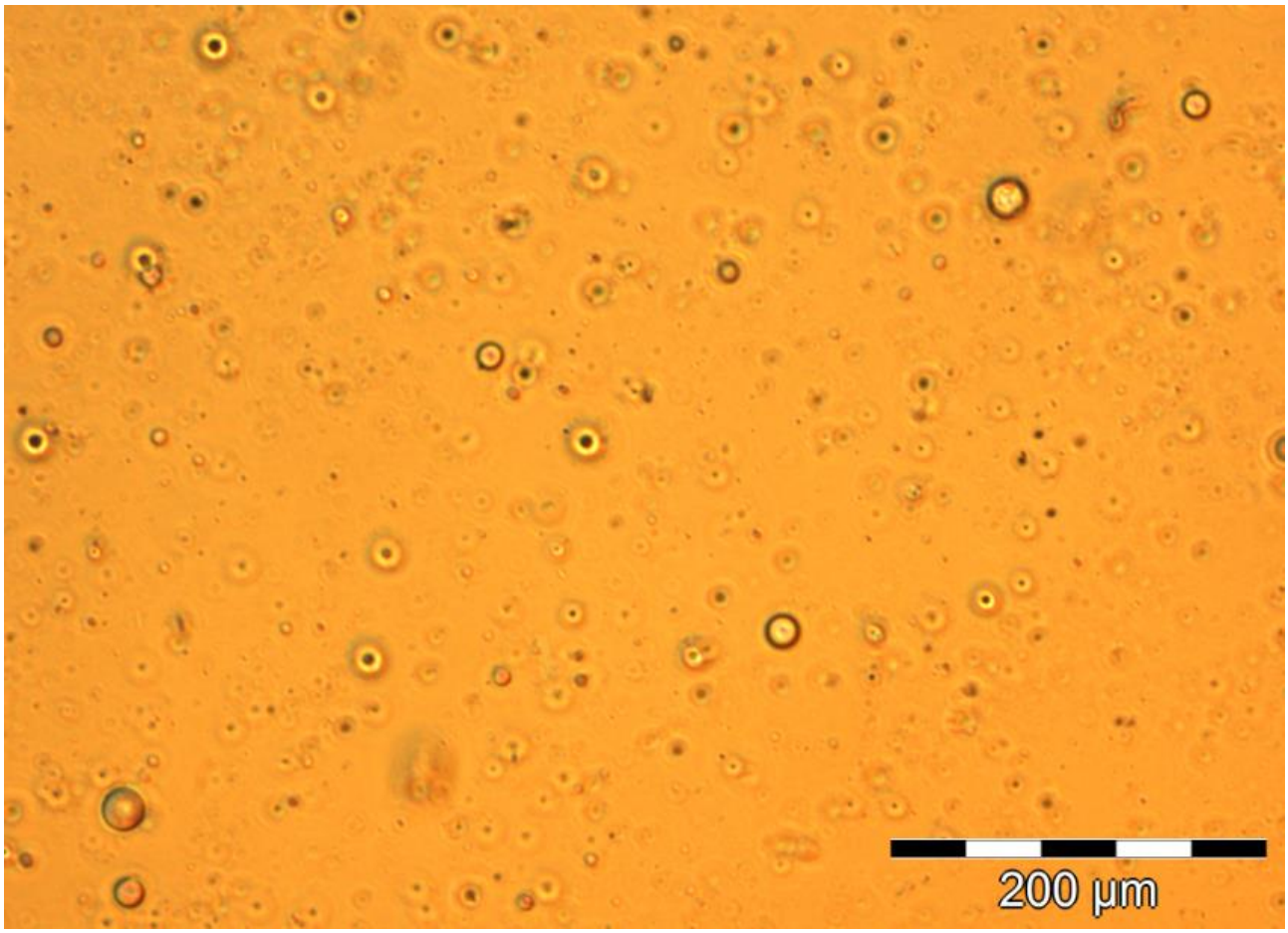


Figure 53. Picture of 10 wt% cellulose into [h-TBDH][OAc] after overnight reaction at 80°C, taken by a optical microscope using polarized light. The solution is clear and no crystals are observable. The round spots are air bubbles due to viscosity.

Synthesis of a new superbase structure: BTM-mTBD.

Synthesis of the triamine precursor.

Another interesting method consists to start the reaction with cheap starting material as isobutyraldehyde and paraformaldehyde to end up with an alkylated dioxime. This type of function can be reduced to primary amine by hydrogenation using high pressure and a Parr reactor.

Two reductions have been tried, the first one using classic Raney nickel at 1200 PSI overnight, the pressure in the reactor decreases to 1186 PSI, the product is a clear oil containing solid. The solid is the starting material, after NMR analysis the oil shows a product with high purity and a yield around 65%. The second reduction is done with a Raney nickel containing activated Mo (Molybdenum), compared to the classic catalyst this one is more reactive. The pressure in the reactor decreased

from 1080 PSI to 997 PSI during the night. This time less solid is observable and the yield is higher (85%).

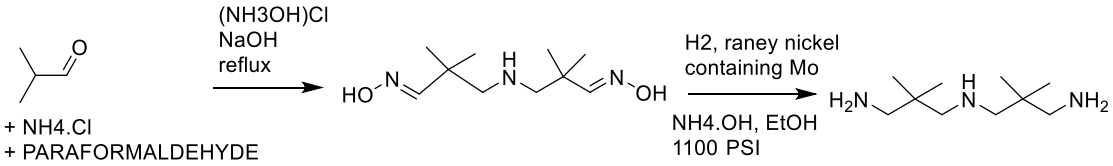


Figure 54. Synthesis of BTM-mTBD triamine precursor

Procedure:

In a 2 L flask, add 33.4g of NH4Cl, 100g of isobutyraldehyde, 45g of paraformaldehyde, 20.0 ml water, and 1.0 ml of HCl, are stirred for four and half hours. While the reaction was boiling, a solution of 100g of $NH_2OH.HCl$, 1.3l of EtOH and 400ml of water were added over a period of half an hour and reflux for 1h. The reaction was then cooled down at room temperature and stored in a freezer overnight. The day after the product was filtrated and washed with ethanol, then dried with rotavapor. Yield 70%.

Before the reduction by hydrogenation, the dioxime needs to be deprotonated because the functions have to be available to undergo this reaction:

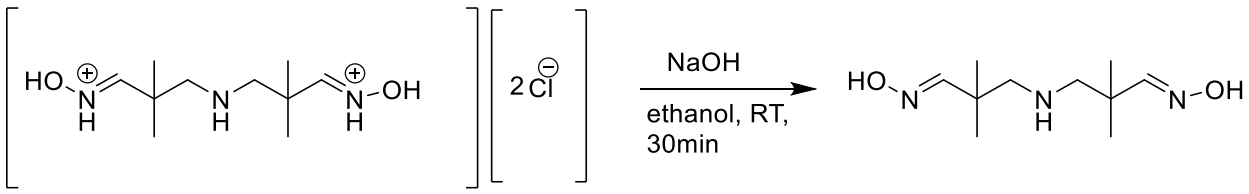


Figure 55. Neutralisation of the dioxime as a salt to obtain a free dioxime before reduction using hydrogen.

Procedure:

In a 500ml RBF add 20g of doxime in 130ml of EtOH, 65ml of a 1M NaOH solution were added under argon atmosphere, stirred for half an hour. The deprotonated dioxime was then extracted with

dichloromethane, the organic phase was dried over Na_2SO_4. The solvent was evaporated and the product was dried under high vacuum.

The reduction takes place in Parr Reactor equipped with a stirrer and 100 ml of ethanol, 50 ml of a 14.8 M solution of ammonium hydroxide, 2ml of Raney nickel containing activated Molybdenum. The temperature was set up at 100°C, and the pressure at 1100 PSI, the mixture was stirred overnight. The product was filtrated and dried with a rotavapor. Yield 85%.

Figure 56. Parr reactor used to reduction the dioxime into a triamine.

Even if the reaction gives a good yield, one objective is to increase it. This can be done by synthetizing fresh catalyst or changing the amount of solvent.

Ring formation.

The cyclisation can be done using guanidine salt or TMG.HCl, it requires at least 8h of reaction but can let be reacting overnight. During the reaction NH_3 gas is released, guanidine.HCl is a salt so

cannot evaporate and the triamine has a boiling point higher than 250°C so the experiment can be done in an open RBF. With this type of cyclisation the product is pure enough to be used for further reaction without distillation or other purification technique

Procedure:

In a RBF of 50 ml 3,17g of 1,3-Propanediamine (0,017 mol, 1equivalent) and 1,6g of guanidine.HCl (0,017 mol, 1equivalent) were charged and heated at 155°C with slow agitation. After 30min ammonia was released, the reaction was kept under stirring for 8h. The mixture was cooled down to 60°C and 20ml of methanol were added. In a Becker, a 20ml solution of NaOH in methanol was prepared (0,017 mol, 1equivalent) and added slowly to obtain the product as a free base. The solvent was dried using a vacuum and a solid was obtained. The product was extracted two times with 30 ml of DCM and evaporated. Yield: 93%

Figure 57. Picture of the BTM-TBD recrystallized from toluene.

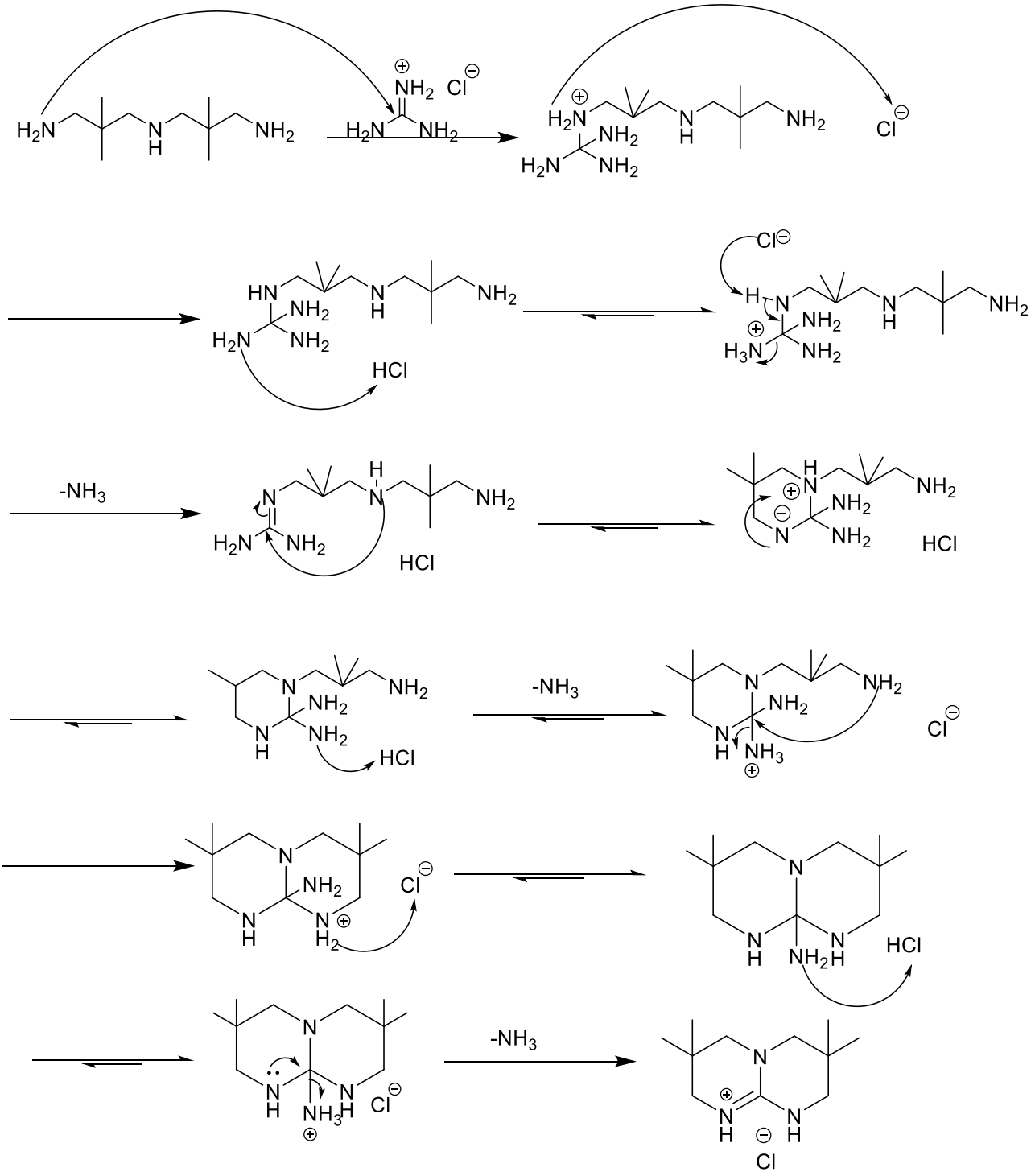


Figure 58. Cyclisation mechanism of the triamine to obtain a bicyclic guanine base as a salt

Synthesis of BTM-TBM derivatives.

The aim of this part is to synthetize new superbases using the TBD derivative made previously, a way to do this is to follow the same procedure used to synthetize alkylated TBD. The alkylation has been done to form the methyl, allyl, and hexyl derivative. All of them need to be distil before further reactions.

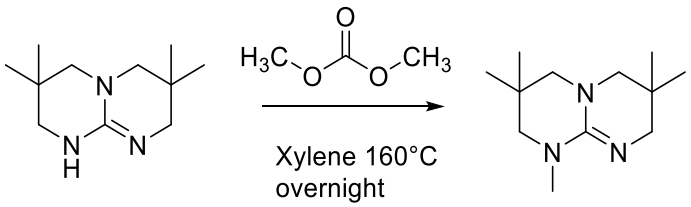


Figure 59. Methylation of BTM-mTBD

Procedure:

Into a two necked 100 ml round bottomed flask 0,2g (0,001mol, 1 Equivalents) of TBD were charged and dissolved in 0,27g (0,003moles, 3 Equivalents) of DMC were added dropwise under reflux. The reaction mixture was kept at reflux under vigorous stirring overnight. Then the crude product was filtered. Finally, the solvent was removed under vacuum. An orange liquid was obtained, yield= 65%. This crude product needs to be distilled before any other reaction, using a Kugelrorh with a vacuum of 0,8 mbar at 160°C. White crystals are obtained.

About the Allyl and Hexyl derivatives, the reaction conditions are the same used for making h-TBD and A-TBD. Both of them in a first time are tried at room temperature during 48H. As the reactions work, now the goal is to optimise the yield by changing the conditions of reaction (e.g: using 60°C instead of room temperature, changing equivalent equilibrium)

Figure 60. Picture of the crystalized BTM-mTBD

Procedure:

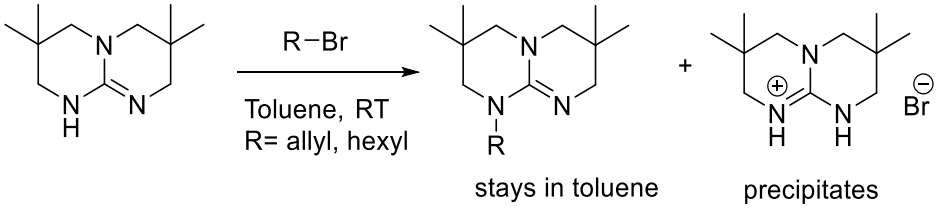


Figure 61. Other alkylation of BTM-mTBD

In a RBF of 25ml 0,2g of beta-TM-TBD (0,001 mol, 1equivalent) were charged with 15ml of toluene, a heatgun was used to help the solubilisation. Once the mixture fully clear, 0,121ml of allylbromide (0,001 mol, 1equivalent) were added all in once, the reaction was stirred during 48H at room temperature:. The solvent was dried and a colourless liquid was obtained. Yield=60%. The solid out of solution can be isolated and recycled for another alkylation reaction.

Synthesis of New ILs based on BTM-mTBD and cellulose dissolution tests.

The first IL is made from AA and methyl-beta-TM-TBD it colourless oil at room temperature. As this reaction is exothermic, it can be cooled down with an ice bath and with a argon flow to avoid contact with the moisture contained in air, which would lead to hydrolysis of the IL.

Procedure:

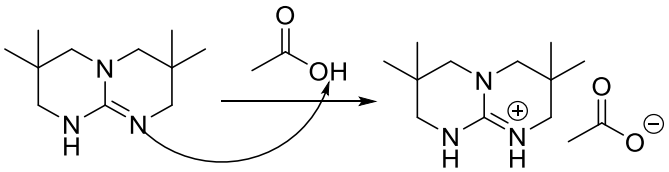


Figure 62. Synthesis of the BTM-TBD based ILs

Into a 10ml RBF 5g of methyl-beta-TM-TBD were charged, equimolar amount of AA is added; the reaction mixture was stirred at room temperature during 1H.

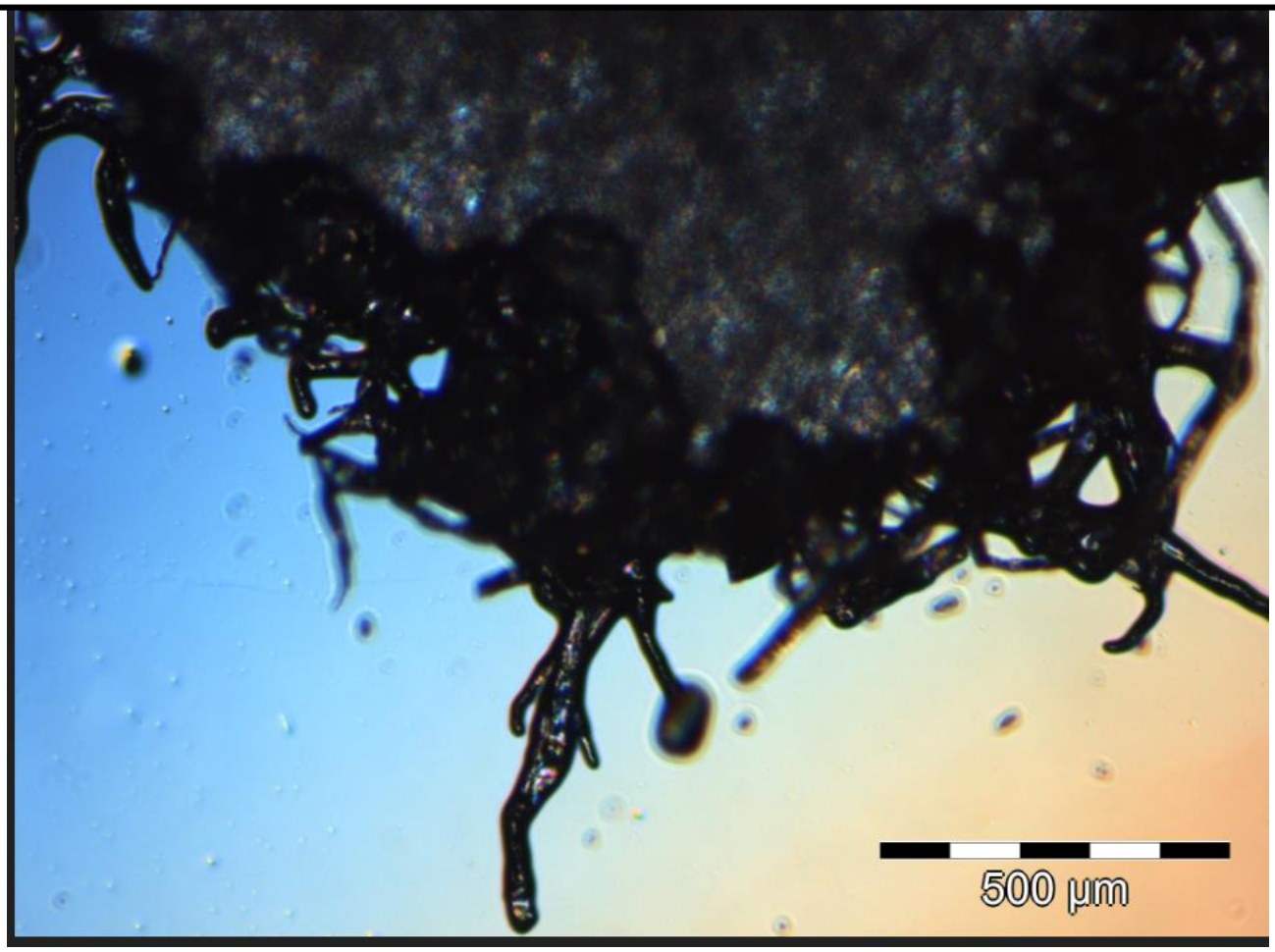


Figure 63. 2 wt% Enocell in DMSO where it is not soluble, this picture is taken with an optical microscope using polarized light as a reference for cellulose dissolution.

The first cellulose dissolution test was done in a 1ml vial using 0,19g of IL and 0,01g of MCC to form a 5wt% solution IL: cellulose. The mixture was stirred at room temperature during 2h, after this the solution was fully clear and still liquid, a microscopic imaging and NMR analysis show that the MCC was fully soluble.

The second cellulose dissolution test was done in a 4ml vial using 0,9g of IL and 0,1g of Enocell to form a 10 wt% solution IL: cellulose. After stirring overnight at 60°C no dissolution was observable.

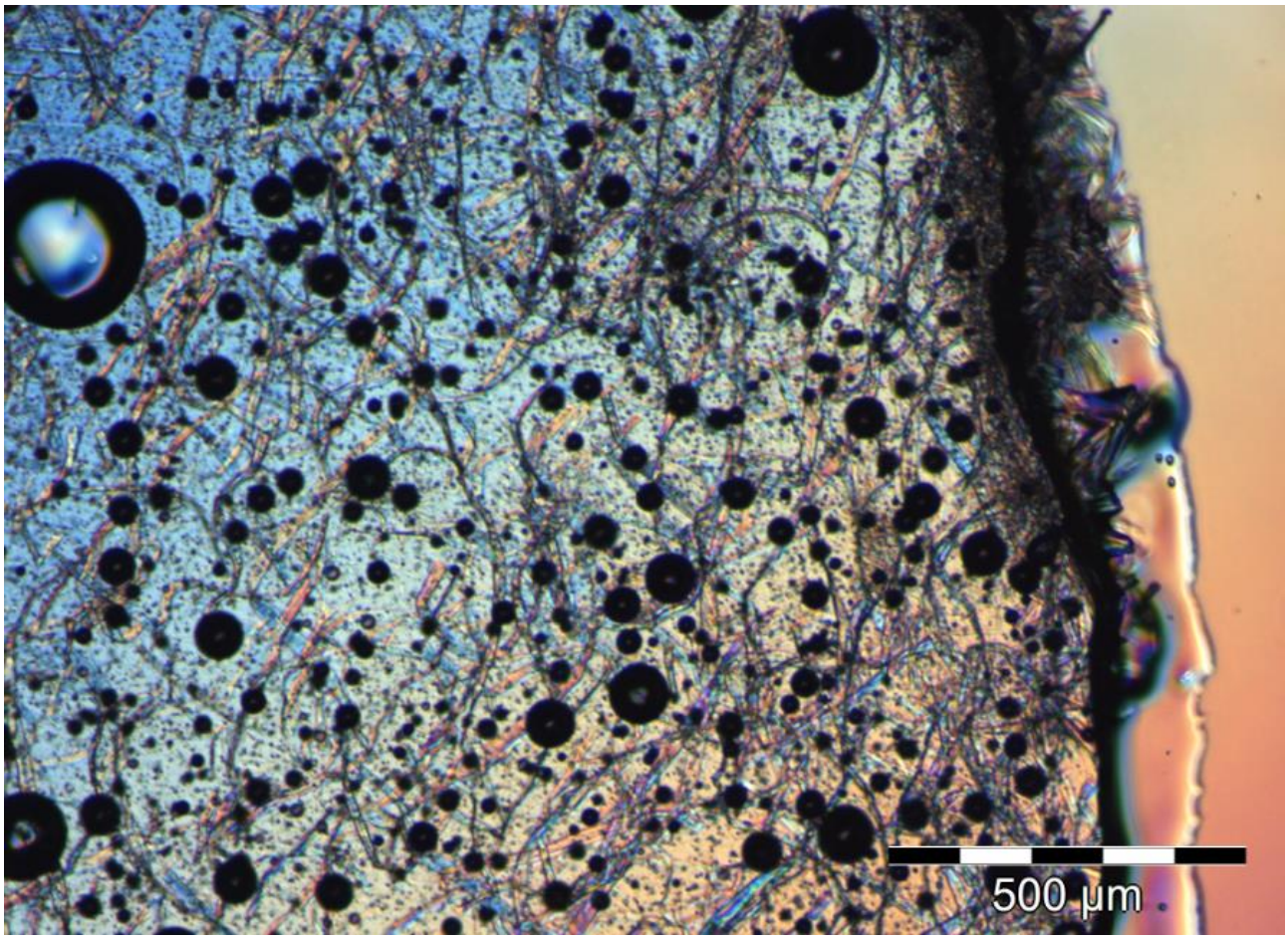


Figure 64. 10 wt% cellulose/ BTM-mTBD overnight at 80°C. No dissolution is observable and no swelling, black spots are air bubbles.

To understand if this comes from the viscosity of the dope or the nature of the IL itself, the experiment was repeated using in addition 10 wt% of DMSO as a co-solvent. After 30 min of reaction at 60°C the mixture became a clear colourless viscous oil. The cellulose was fully dissolved. This was prouved by microscopy imaging.

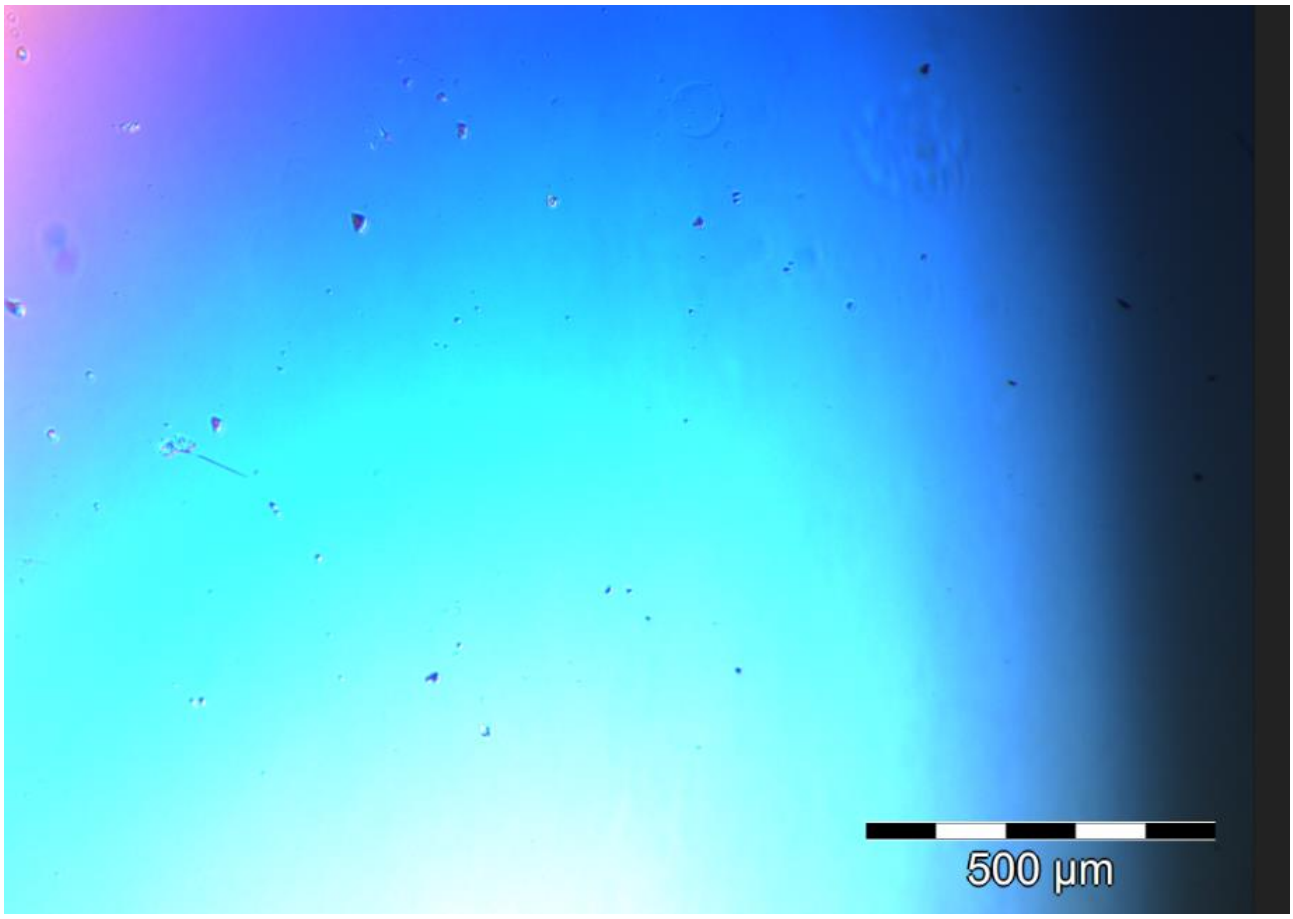


Figure 65. 10 wt% cellulose/ BTM-mTBD/ 10wt% DMSO after two hours at 80°C. No fibre left, the cellulose is fully dissolved.

Now the concentration in cellulose has to be increased to see how much the IL is able to dissolve, but also the other IL based on BTM-TBD derivatives have to be test as solvent for cellulose. Different types of cellulose have to be test also and the characterisation of the compounds such as hydrolytic stability, thermal stability…

The work about synthetizing new triamine to form new superbases is still ongoing such as the other derivatives have not been tested and many other bicyclic structures have to be investigated.

Synthesis of triamines precursors for TBD-alternatives:

All the previous TBD derivatives were synthetized starting from TBD itself and alkylated at the nitrogen position, but it is also possible to alkylate the carbon contained in the ring of TBD. In this case, the alkylation must be done before the ring formation. The triamine can be formed by addition of halogenated primary amine and a diamine. The major challenge in this part was to alkylate and

synthetize a halogenated primary amine starting from a cheap compound. A first good try was to use ethyl cyanoacetate, the two protons in alpha position are acidified by the electron withdrawing effect from the cyano-group. They are easily removed by a base, this make the position favourable for a methylation. A first methylation was tried using MeI but this leads to mixture of mono and di-methylated compounds and requires a distillation to obtain only the dimethylated compound. The second methylation is made by using dimethyl sulfate which is a strong methylating agent after the first methylation the second proton left is even more acidic, so a second methylation occurs (Figure 66). Once the methylation done, the ester and the cyano-group can be reduced to alcohol and primary amine by using a hydride. LiAlH4 is the best choice in this case because it is one of the most powerful hydride-transfer reductant, it is less toxic than Boron Hydride and it reduces ester easily and cyano-group slower but still in a high yield (up to 80%).

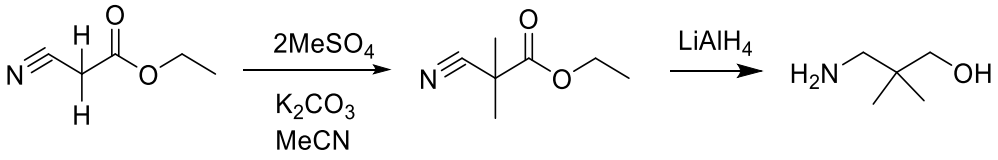


Figure 66. Synthesis of 1-Propanol, 3-amino-2,2-dimethyl-

The next step of this reaction would be to form a triamine by adding a diamine, but the alcohol is not a good leaving group. So, a group substitution is needed (Figure 67). Replacing the OH group by a bromide is easily done by dissolving the amino alcohol in hydrobromic acid (48%) and reflux it overnight.

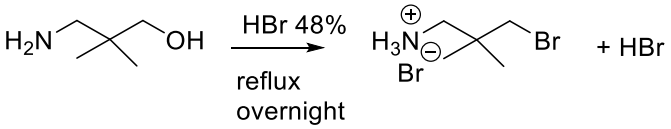


Figure 67. Synthesis of 1-Propanamine, 3-bromo-2,2-dimethyl-, hydrobromide

After drying the solvent the product is obtained as a salt so as a white solid which can be solubilized in an excess of diamine.

After the reaction a mixture of triamine and diamine is in the flask, due to high difference of boiling point distillation can separate them. The main issue with this reaction is the yield (Figure 68).

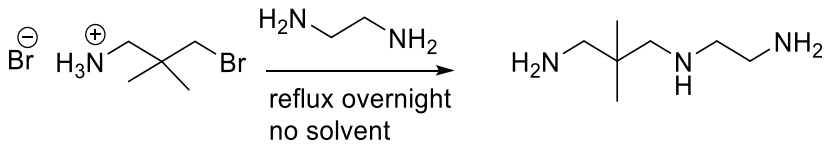


Figure 68. Synthesis of triamine precursor for TBD derivative

Procedure:

In a 500ml RBF 69g of potassium carbonate, 28,2g of ethyl cyanoacetate and 2 equivalents of dimethyl-sulfate (47,4ml) in 300 ml of acetonitrile and were refluxeed at 90°C during 48h. The product was then filtrated, and the solvent evaporated. Yield 81%.

The reduction into amino-alcohol was made in a 500ml RBF with 300ml of THF and 10 equivalents of LiALH4. The excess of hydride was quench with water dropwise, the product was filtrated, and the solvent evaporated. Yield: 80%

The bromination of the amino-alcohol took place in a 100ml RBF, 3g of amino-alcohol was used and 4 equivalents of hydrobromic acid were added (14ml) without solvent and refluxed overnight. Yield: 61%.

The reaction gave colourless liquid containing small particles, they were filtered off and the liquid distilled. The NMR spectra shows a diamine spectra with a low concetration of triamine.

As the previous experiment gave a low yield, an alternative method consists of starting by bromination of neopentylglycol (Figure 69). The goal was to instead of first doing the methylation, then the bromination; was to first do a bromination then do an nucleophilic substitution. The first step consists of protonation of an alcohol group using acidic conditions, this will lead to water and goes through a SN_2 mechanism. The bromide from the hydrobromic acid is a good nucleophile so the bromination is favourable. A reaction of substitution is a reversible process, but because of the acidic condition the equilibrium is more favourable for the bromination than the hydroxylation, as the HBr is a strong acid (pKa= -9) so it is dissociated in [$H3O^+$] [Br^-] and the halide is already free to react. The hydroxyl group is release as a water molecule, and this is a weaker nucleophile than bromide. The molecule is symmetrical so there is no selectivity between the two alcohol groups so double substitution occurs To be sure that the conditions are acidic enough to push the equilibrium

to the brominated compound, trifluoro-methanesulfonic acid is used as a catalyst to increase the acidity (5% of total volume).

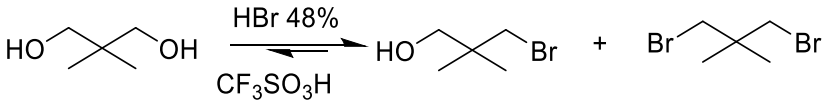


Figure 69. Bromination of 1,3-Propanediol, 2,2-dimethyl

After the bromination, neutralization of the HBr in excess is needed before drying the solvent. The main problem with this reaction is the yield. Before acid neutralization the NMR spectra shows a double bromination. However, after the work up the NMR shows mono-, di- and unbrominated compounds (Figure 70). During the neutralisation, the bromide is removed, and the hydroxide anion takes place, so the yield decreases.

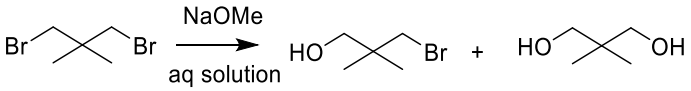


Figure 70. neutralisation of HBr in excess from bromination of 1,3-Propanediol, 2,2-dimethyl-

NaOMe is a nucleophilic base so this explain why the product goes back to the starting material, a way to avoid this is to use a non-nucleophilic base strong enough to neutralise the excess of hydrobromic acid in a convenient added volume. More than one choice are possible: LDA, DIPA, Na-t-BuOH, t-BuOK. But all of these react violently with water, are pyrophoric, explosive and toxic, as the reaction occurs in aqueous phase they are not suitable for this case. An alternative is to use a superbase: they are strong base in aqueous phase, non-nucleophilic, less or non-toxic and do not react violently with water many choices are also possible: TBD, DBN, DBU, m-TBD, h-TBD... One problem could be the hydrolysis of the base so the choice will be m-TBD as it is the most stable in water.

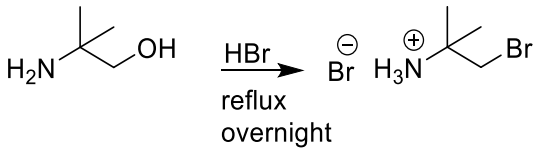


Figure 71. Bromination of 2-Propanol, 1-amino-2-methyl

Procedure:

In a RBF of 25ml, 2ml of 1-Propanol 2-amino-2-methyl (0.02 mol, 1 equivalent) were charged and cooled down with an ice-bath, 10ml of hydrobromic acid (0.05 mol, 2,5 equivalents) were added dropwise, once the acid-base reaction between the HBr and the anime function over, the mixture was stirred at room temperature for 5min and reflux overnight. The day after 14,6ml (17.23g, 0,11 mol) of m-TBD were needed to neutralize the excess of HBr, pH was followed all along the neutralization by pH-paper until it is neutral. The aqueous phase was dried and an orange viscous oil containing the product and [m-TBDH][Br]. This was dissolved in 20ml of ethanol; 45ml of toluene was added and stirred to one hour. After evaporation of the solvent a colourless oil appeared, after more distillation using a Kugelrohr operator a white solid was obtained.

NMR analysis reveals that the m-TBD reacted with the product itself and not only the acid and this synthetize a new compound. This explains why even after distillation the wanted product cannot be isolate (Figure 72).

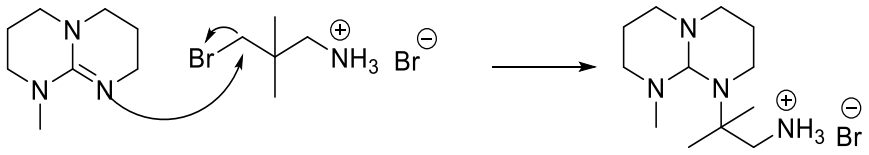


Figure 72. m-TBD reacting with 1-Propanamine, 3-bromo-2,2-dimethyl-, hydrobromide

An alternative to this is to use a weaker non-nucleophilic base such as K_2CO_3, $KHCO_3$ or Na_2CO_3. The best choice between those bases was the $KHCO_3$, as they all form the corresponding nucleophilic base in aqueous solution, the aim was to minimalize this reaction (Figure 73). $KHCO_3$ owns only one oxygen able to be activated to react with the excess of acid, this limits the formation of KOH in solution. These bases are not strong enough to deprotonate the compound itself so the reaction still end up with a salt. This can be used in a positive manner as the addition of a diamine on an amino-bromo compound will lead to a nucleophilic attack from the nitrogen attached to the diamine on the carbon attached to the bromide but also on the one attached to the nitrogen, so polymerization occurs. If the nitrogen is protected because it is a salt, the nucleophilic attack can occur only on the C-Br bond and lead to the wanted product.

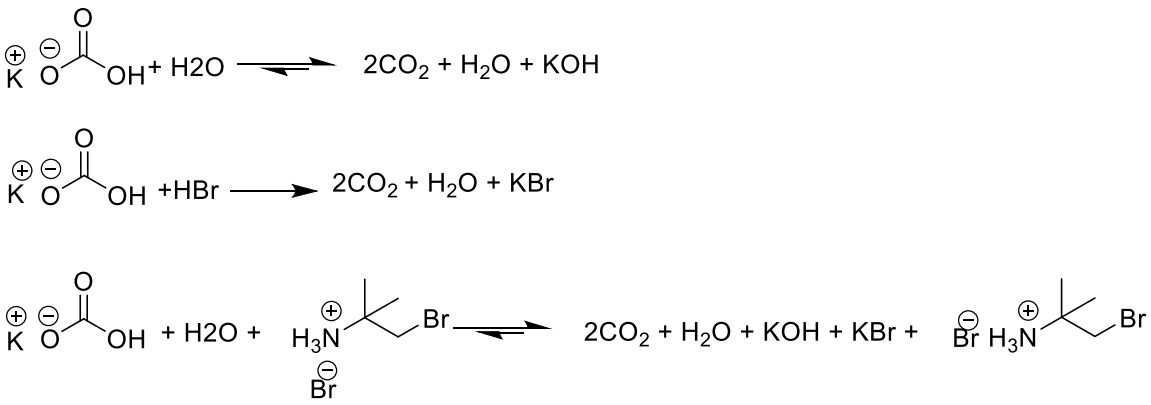


Figure 73. Reaction of $KHCO_3$ with the different species present in the flask during the reaction

After the neutralisation, the aqueous phase was dried using a rotavapour and a white solid composed of $KHCO_3$, KOH, KBr, and the wanted compound was obtained. As the KBr salt is not soluble in ethanol, the objective was to solubilse only the product from the reaction but the KOH base is highly soluble in ethanol; this was not a problem for the next step of the reaction. Immediately after addition of the solvent a white precipitate appeared, the mixture was filtered and the ethanol dried. At the end, a white wet solid was obtained with a yield of 60%.

The compound was ready for the next step; the addition of the diamine is made through a SN2 mechanism. After the reaction, a mixture containing a white solid and a dark yellow liquid was in the flask, to separate them, a centrifuge is used during 30 min.

After NMR of both liquid and solid, it appears that the liquids contains a mixture of a diamine and triamine and the solid appeared to be the wanted product. The liquid can be distilled to purified the excess of unreacted diamine and involve it again in a second reaction using a kugerlrohr connected to a water pump (pressure around 8 mbar instead of 0,4 mbar). The solid was then dried using a rotavapor with a yield of 90%. As this is a salt it needs to be deprotonated before cyclisation.

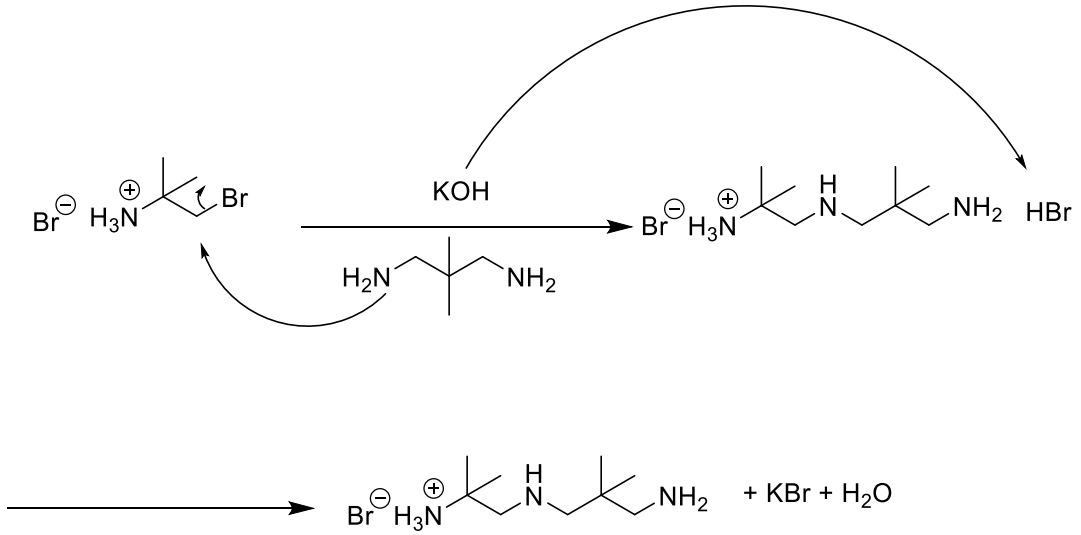


Figure 74. formation of the triamine precursor as a salt

Methyl acrylate is an interesting starting material because the double bond can be brominated by hydrobromic acid without solvent to form Methyl 3-bromopropanoate which has a two acidic proton in alpha position and this allows methylation by dimethyl sulfate. The inconvenient with this reaction is the same as with the neopentylglycol. The reaction ends up with a mixture of products, brominated in alpha or beta position this reduce the yield to 15% and it needs more purification by distillation.

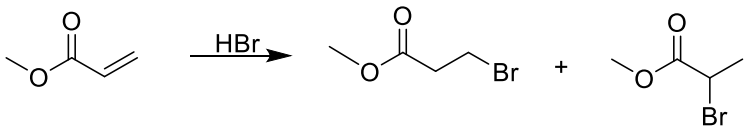


Figure 75. Bromination of methyl acrylate leading to a mixture of two products

Methyl 3-bromopropanoate is a good alternative of ethyl cyanoacetate so another route of synthesis has been tried. Starting from 3-Hydroxypropanenitrile to form 3-hydroxy propanoic acid by using HBr as a reagent and solvent. This reaction gives a high yield (84%). The next step consists is to esterify the carboxylic acid but the major inconvenient here is also the yield.

The reaction is made in methanol with sulfuric acid as a catalyst (5% of the total volume), it will activate the ketone from the carboxylic acid and by delocalisation. The positive charge on the oxygen will move to the carbon and form a carbocation, thus one of the free electron pair on the oxygen from the methanol can attack. This result by the release of water and formation of ester. As we are in acidic conditions the ketone of the ester can be activated and the reverse reaction can occur. An equilibrium between starting material and product is reach the consequence is the yield's decay (around 30%)

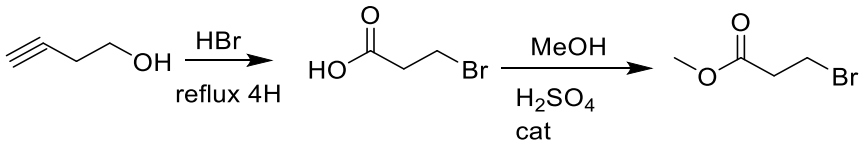


Figure 76. Synthesis of Propanoic acid, 3-bromo-, methyl ester

Conclusion

Cellulose is a promising compound as it exists in a huge quantity, it is biodegradable, natural and find a lot of applications in material and green chemistry. Because of its properties such as big system of hydrogen bonding, cellulose is hard to solubilize and hard to analyse by classical analytical methods. To solve this problem, chemist focused on new polar solvent and ILs appeared to be a good alternative because of their exclusively composed of ions.

Some challenges are still present, even if the cellulose is dissolved, the products obtained are too viscous and can form a dense gel which make the sample impossible to run by NMR as the resolution will be too bad. Also using ILs will complicate the spectra as additional peaks will be visible, the risk of this is to observe overlapping signals coming from the ILs on the cellulose.

To avoid this, deuteration experience can be processed to decrease the peak's intensity from the ILs, the goal was to lead an integral value close to zero, two different ratios of IL: D2O have been used to determined which one would be the most efficient. The experience is run with [P4444][OAc] and the two ratios of IL: D2O are 1:1 and 1:5, the deuteration exchange was observable on the alpha and acetate position, at the end of this work we observe a deuteration more important on the 1:5 so it is defined as the best ratio for deuterium exchange.

A new generation of ILs using superbases is generating a lot of interest as they seem to dissolve cellulose, some exist with TBD and DBU. The aim was to find TBD derivatives and try their capacity on cellulose dissolution, the first derivatization was done on the nitrogen position from the guanidine function. The Hexyl-TBD is able to dissolve cellulose up to 15 wt % at 100°C but it forms a gel so needs to be coupled with d6-DMSO to be used as a NMR solvent, the Ethyl-TBD and Butyl-TBD are not dissolving cellulose. The Allyl-TBD is also able to dissolve cellulose but because of isomerization the spectra is complicated to analyse and a lot of peak from this is overlapping with the cellulose.

Another solution was to synthetize triamine precursors for TBD-derivates, in this case the alkylation was made on the apha position and not on the nitrogen. The synthesis of 1,3-Propanediamine, N^1-(3-amino-2,2-dimethylpropyl)-2,2-dimethyl- is satisfying as it gives a high yield and a high product purity, further studies have to be run to cyclize it.

The pathway using the hydratation of Hydracrylonitrile is interesting as this step gives a high yield and purity, the next step is the dimethyl of the carbon in alpha position and this has not been tried yet. The route using the ethyl cyanoacetate as a starting material is a good alternative as the demethylation is working in high yield and purity such as the reduction and the substitution of the alcohol group by bromide using HBr. The next step is the addition of the diethylamine to form the final triamine, its NMR spectra showed a lot of unreacted diethylamine due to the excess used, to solve this it is possible to distil the product and then try the cyclization.

The synthesis of BTM-mTBD showed to be interesting as it dissolves cellulose up to 10%. The route has to be optimise to obtain better yield and higher purity.

According to these results, more triamine precursors must be studied to synthetize new TBD-derivatives after this it would be interesting to check their effect on cellulose.

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Appendix

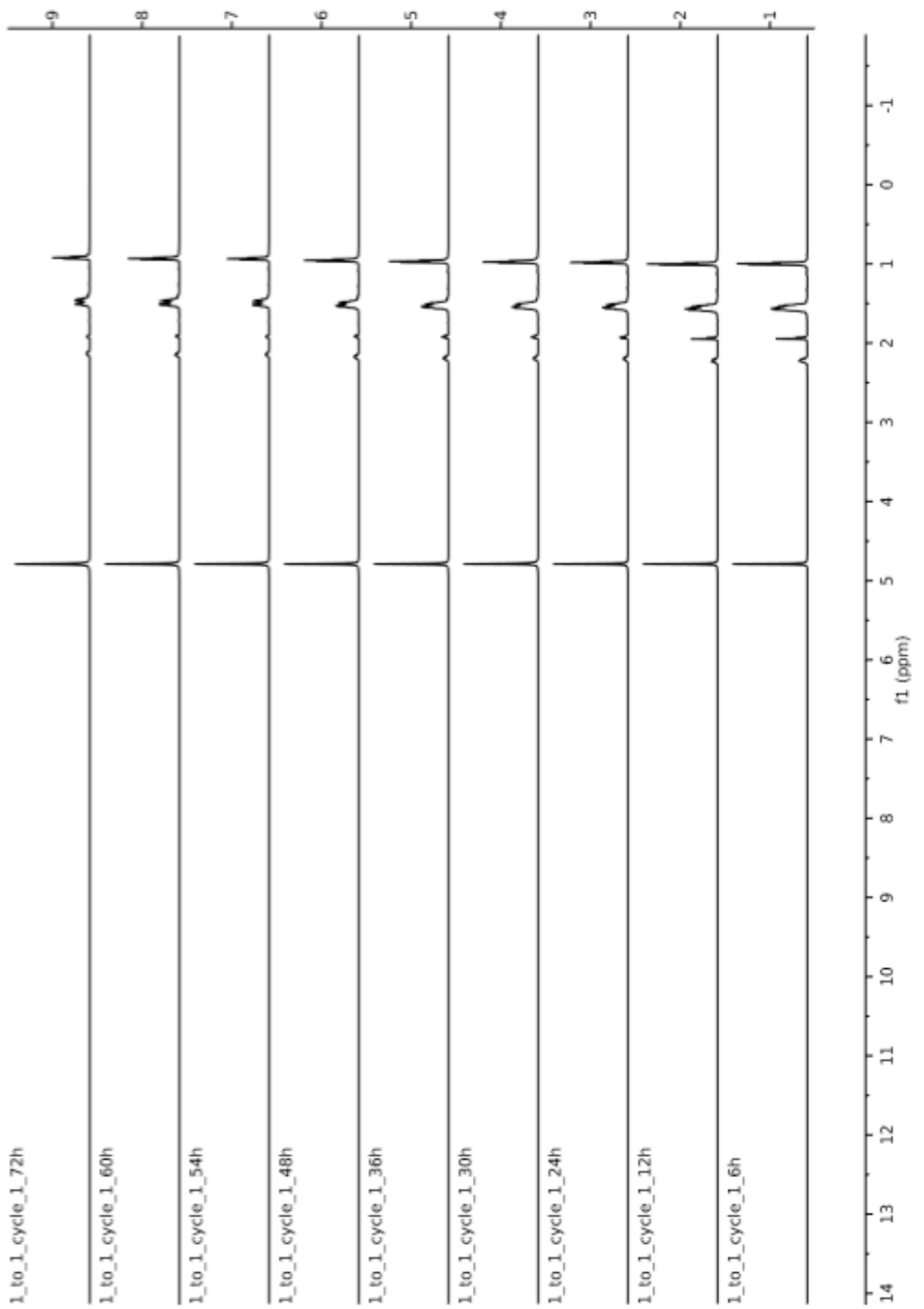

Figure 1. ^{1}H NMR spectra of the first deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH_2-CH_2-CH_3	2.27	8	2.3
P-CH_2-C***H***$_2$-C***H***$_2$-CH_3	1.58	16	16
P-CH_2-CH_2-CH_2-C***H***$_3$	1.02	12	12
Acetate	1.95	3	1.2

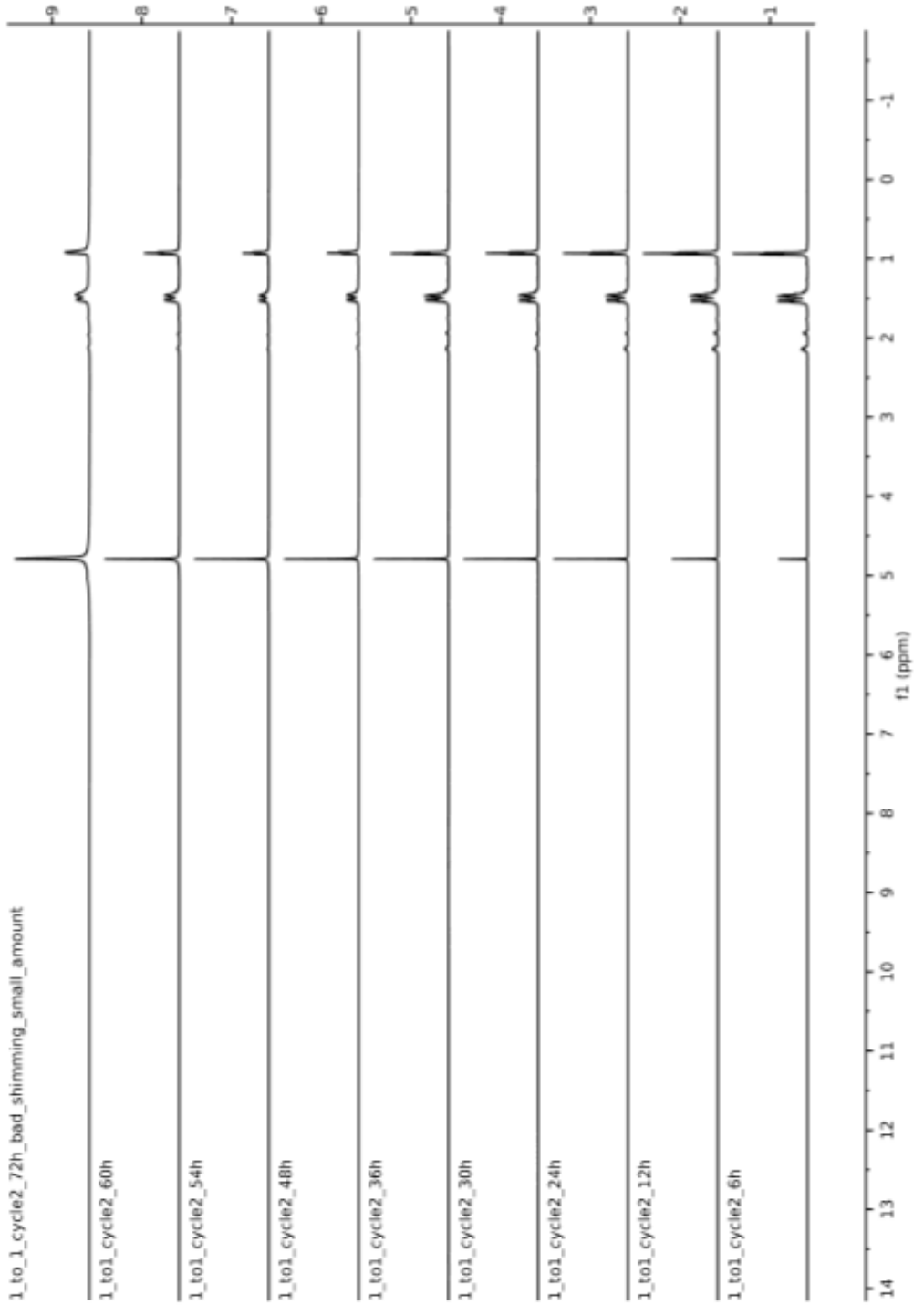

Figure 2. ^{1}H NMR spectra of the second deuteration cycle for $[P_{4444}][OAc]$

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.27	8	0.92
P-CH$_2$-C***H***$_2$-C***H***$_2$-CH$_3$	1.58	16	16
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	1.02	12	12
Acetate	1.95	3	0.35

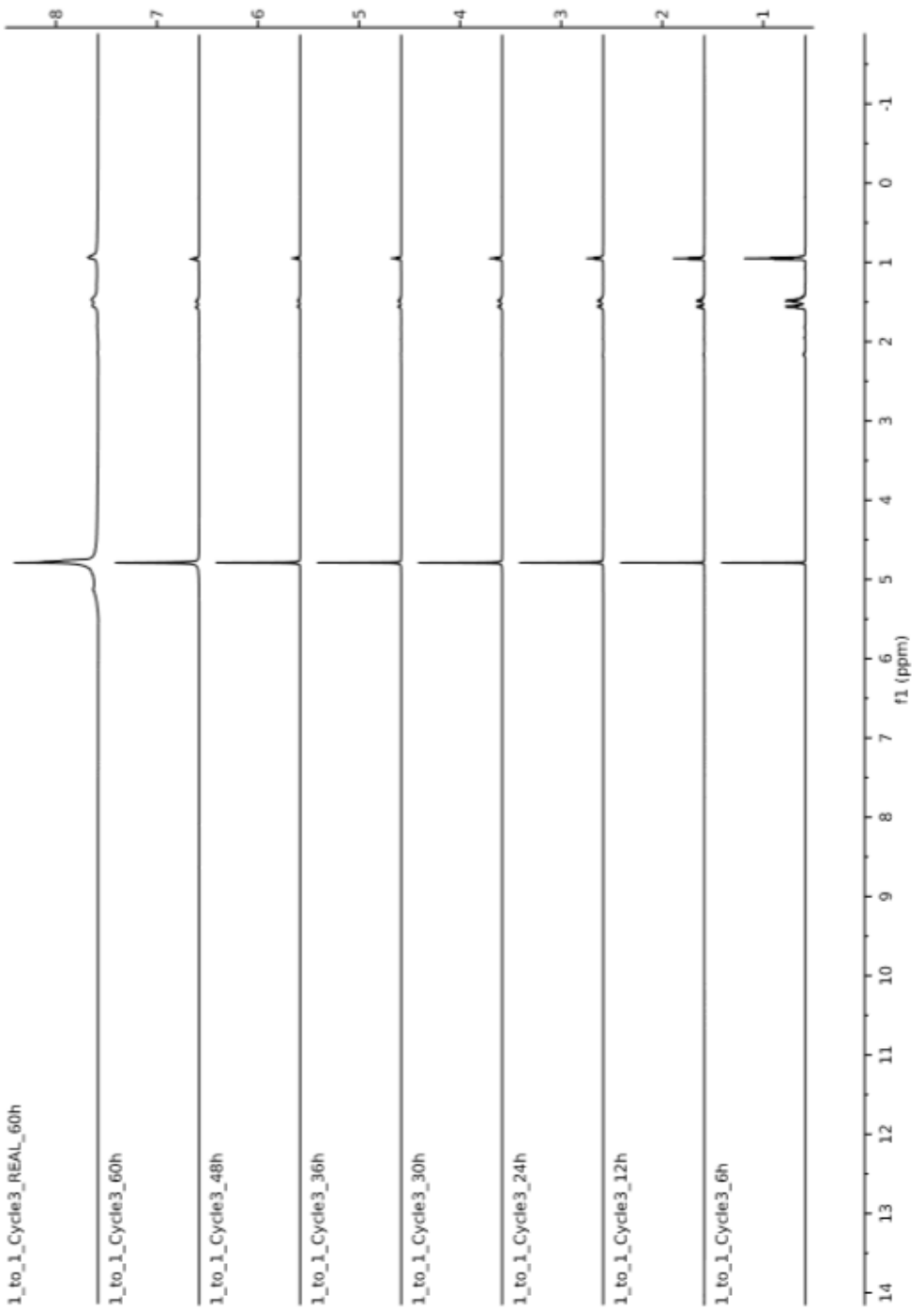

Figure 3. ^{1}H NMR spectra of the third deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.27	8	0.65
P-CH$_2$-C***H***$_2$-C***H***$_2$-CH$_3$	1.58	16	16
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	1.02	12	12
Acetate	1.95	3	0.23

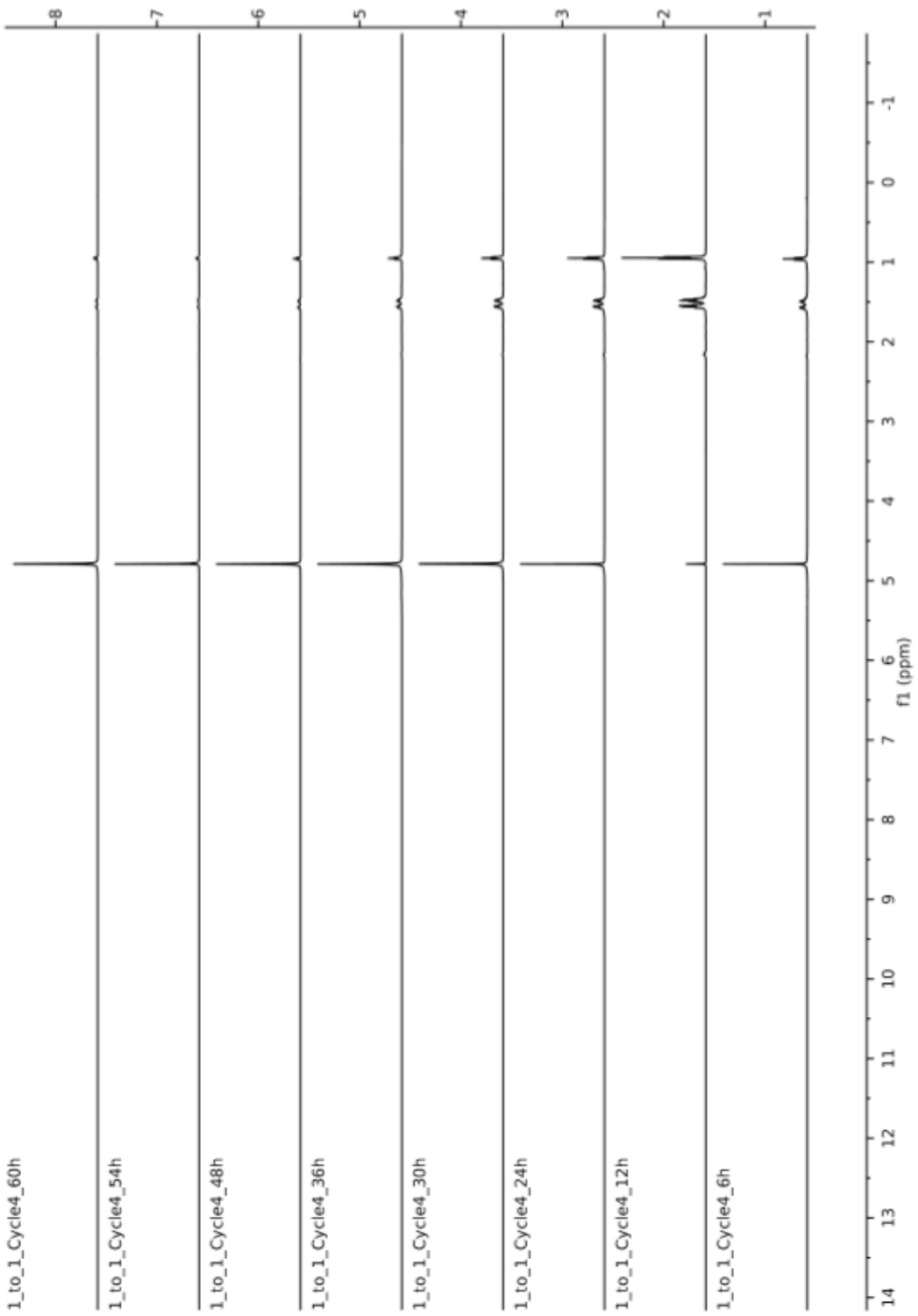

Figure 4. ^{1}H NMR spectra of the fourth deuteration cycle for $[P_{4444}][OAc]$

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.27	8	0.7
P-CH$_2$-C***H***$_2$-C***H***$_2$-CH$_3$	1.58	16	16
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	1.02	12	12
Acetate	1.95	3	0.12

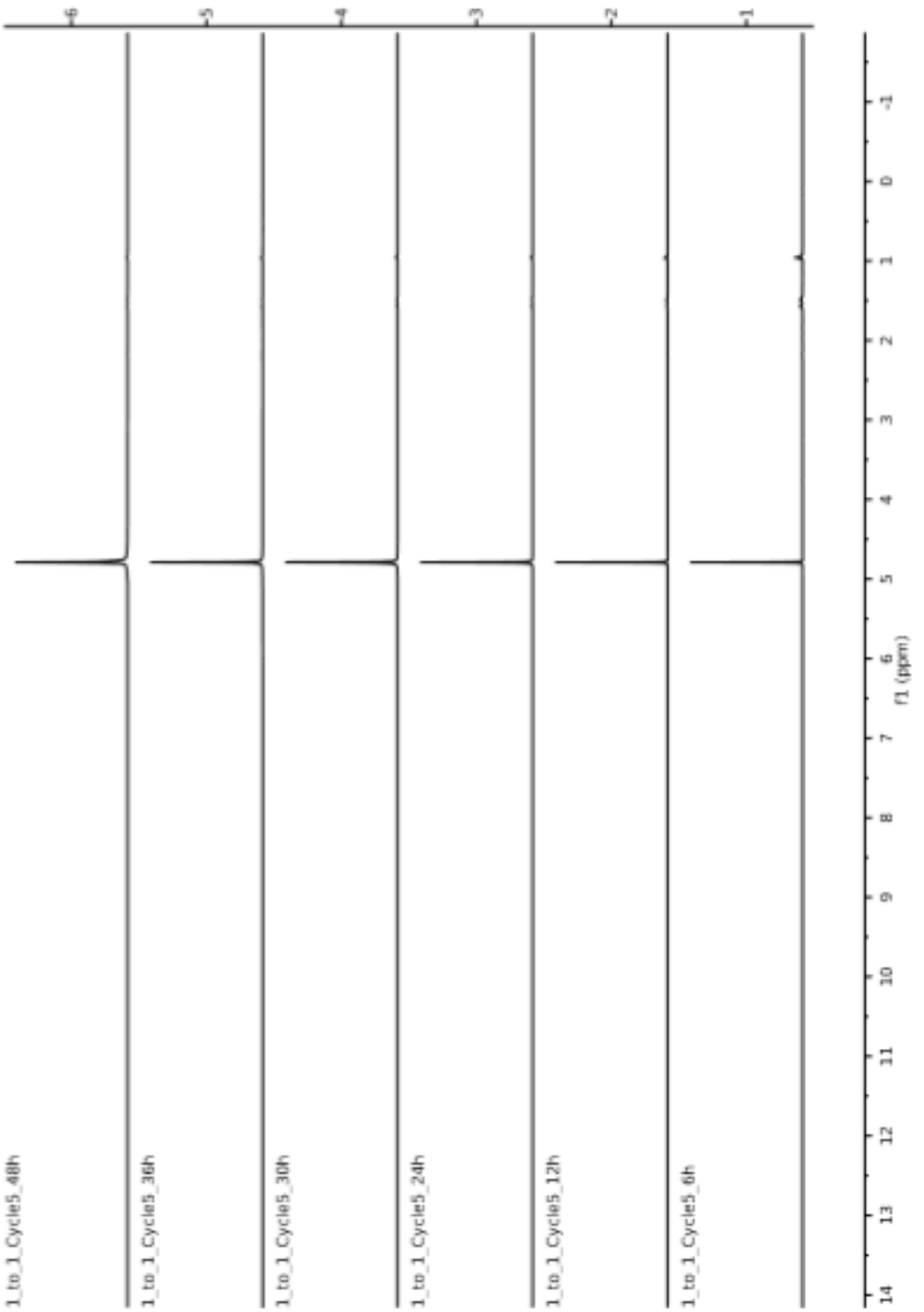

Figure 5. ^{1}H NMR spectra of the fifth deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.27	8	0.68
P-CH$_2$-C***H***$_2$-C***H***$_2$-CH$_3$	1.58	16	16
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	1.02	12	12
Acetate	1.95	3	0.12

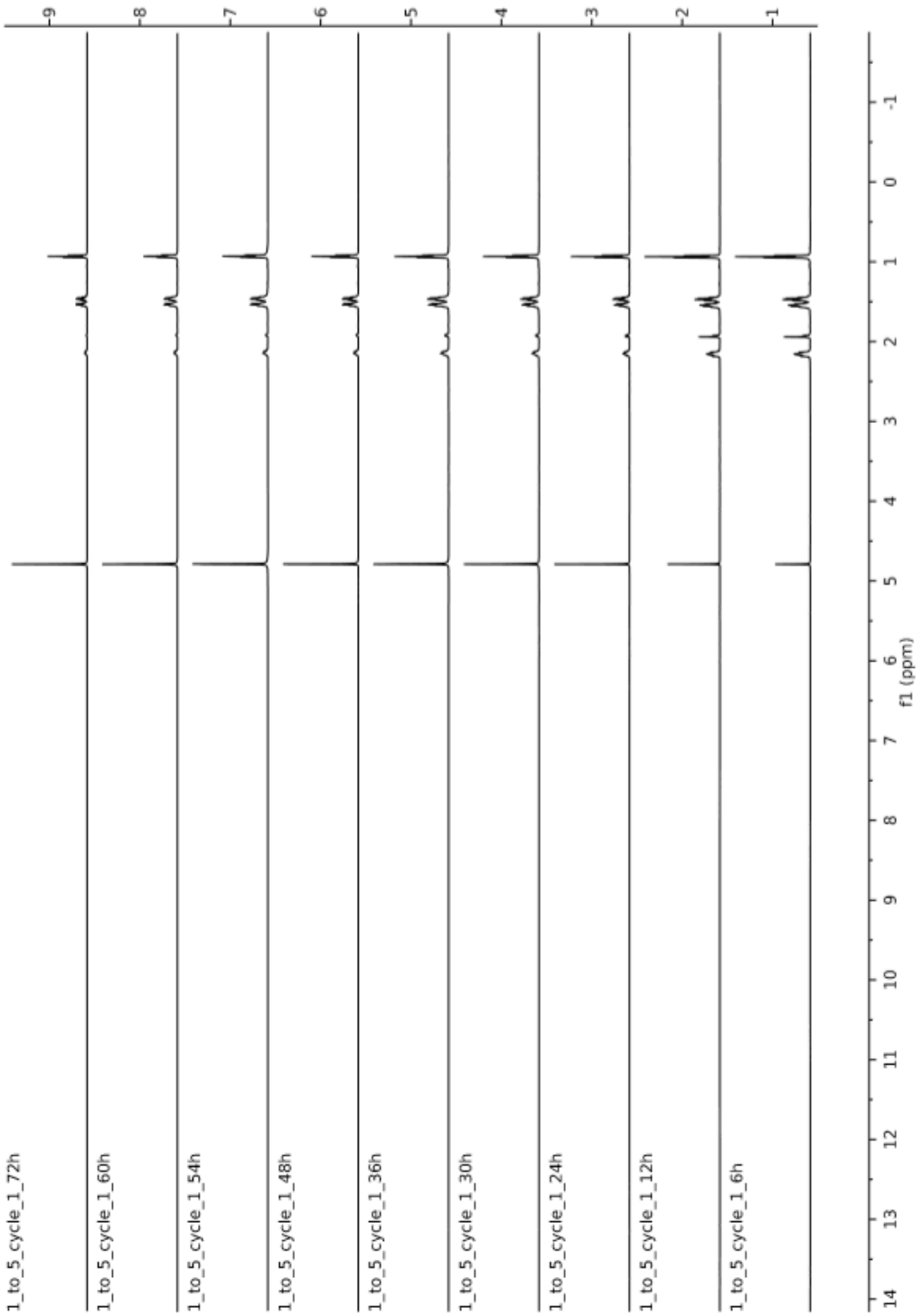

Figure 6. ^{1}H NMR spectra of the first deuteration cycle for $[P_{4444}][OAc]$

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH_2-CH_2-CH_3	2.16	8	2.43
P-CH_2-C***H***$_2$-CH_2-CH_3	1.54	8	8
P-CH_2-CH_2-C***H***$_2$-CH_3	1.47	8	8
P-CH_2-CH_2-CH_2-C***H***$_3$	0.94	12	12
Acetate	1.96	3	0.57

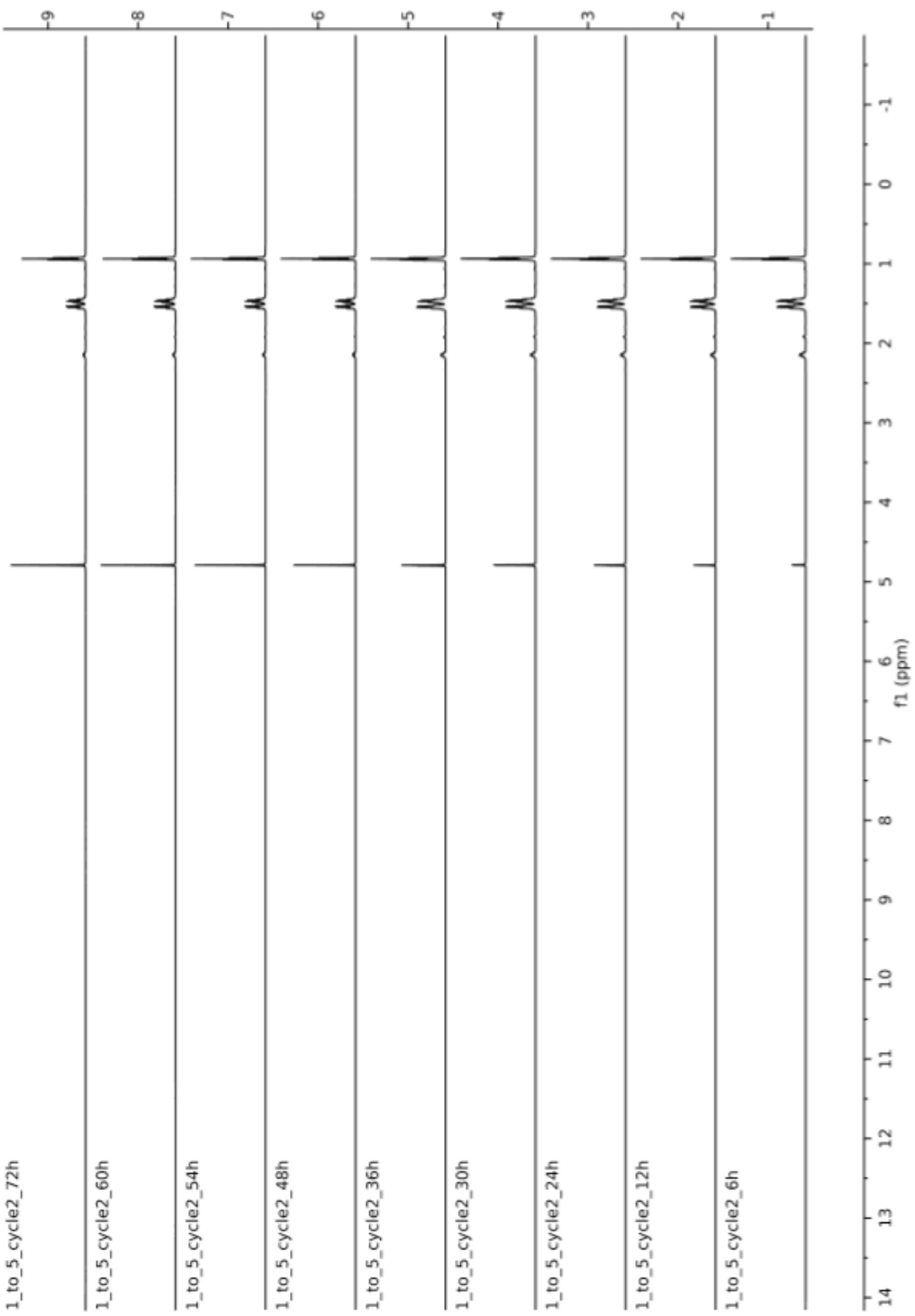

Figure 7. ^{1}H NMR spectra of the second deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.16	8	1.42
P-CH$_2$-C***H***$_2$-CH$_2$-CH$_3$	1.54	8	8
P-CH$_2$-CH$_2$-C***H***$_2$-CH$_3$	1.47	8	8
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	0.94	12	12
Acetate	1.96	3	0.18

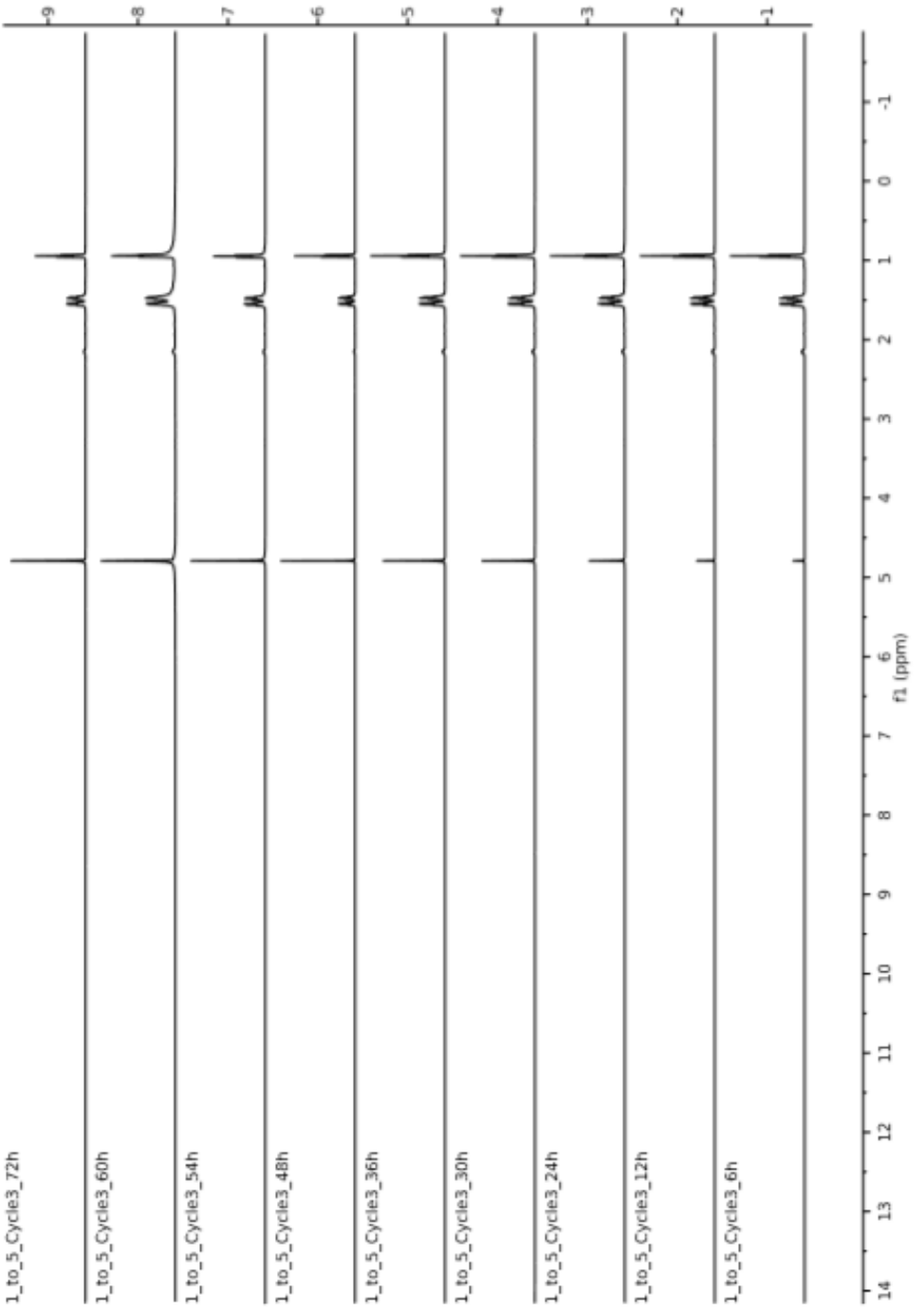

Figure 8. ^{1}H NMR spectra of the third deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.16	8	0.81
P-CH$_2$-C***H***$_2$-CH$_2$-CH$_3$	1.54	8	8
P-CH$_2$-CH$_2$-C***H***$_2$-CH$_3$	1.47	8	8
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	0.94	12	12
Acetate	1.96	3	0.07

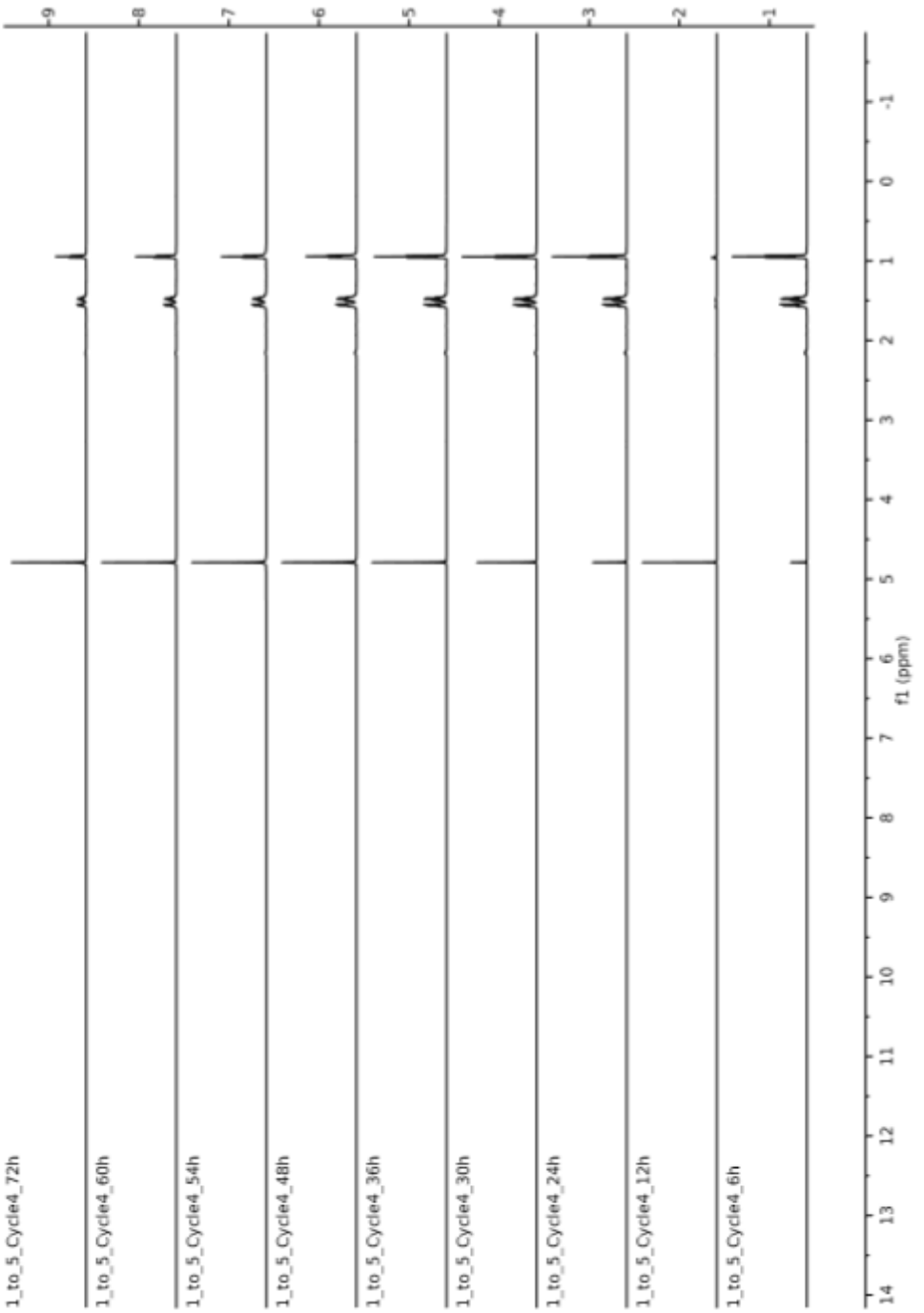

Figure 9. ^{1}H NMR spectra of the fourth deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.16	8	0.62
P-CH$_2$-C***H***$_2$-CH$_2$-CH$_3$	1.54	8	8
P-CH$_2$-CH$_2$-C***H***$_2$-CH$_3$	1.47	8	8
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	0.94	12	12
Acetate	1.96	3	0.04

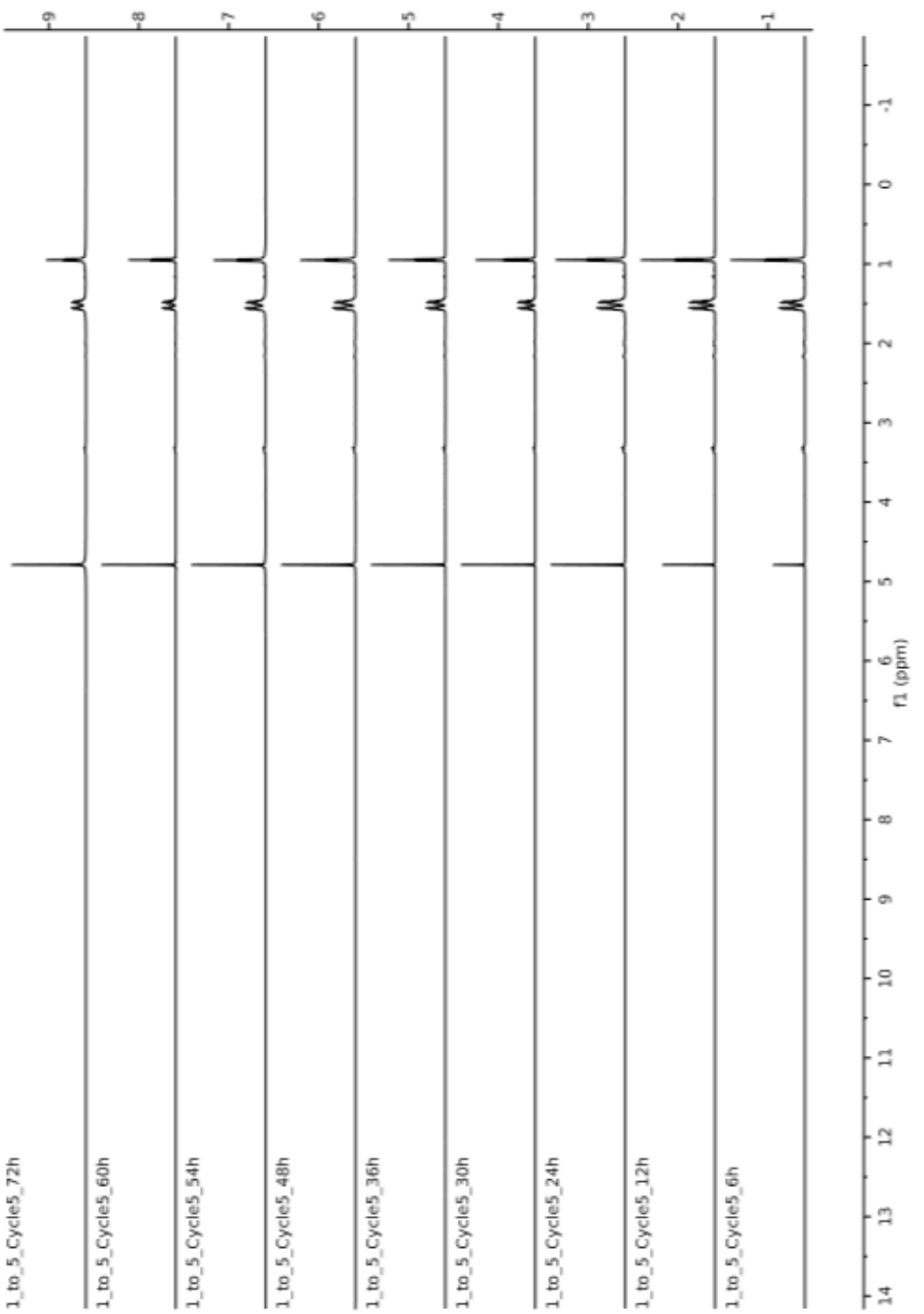

Figure 10. ^{1}H NMR spectra of the fifth deuteration cycle for [P_{4444}][OAc]

Proton	Ppm values	Initial value	72h
P-C***H***$_2$-CH$_2$-CH$_2$-CH$_3$	2.16	8	0.23
P-CH$_2$-C***H***$_2$-CH$_2$-CH$_3$	1.54	8	8
P-CH$_2$-CH$_2$-C***H***$_2$-CH$_3$	1.47	8	8
P-CH$_2$-CH$_2$-CH$_2$-C***H***$_3$	0.94	12	12
Acetate	1.96	3	0.04

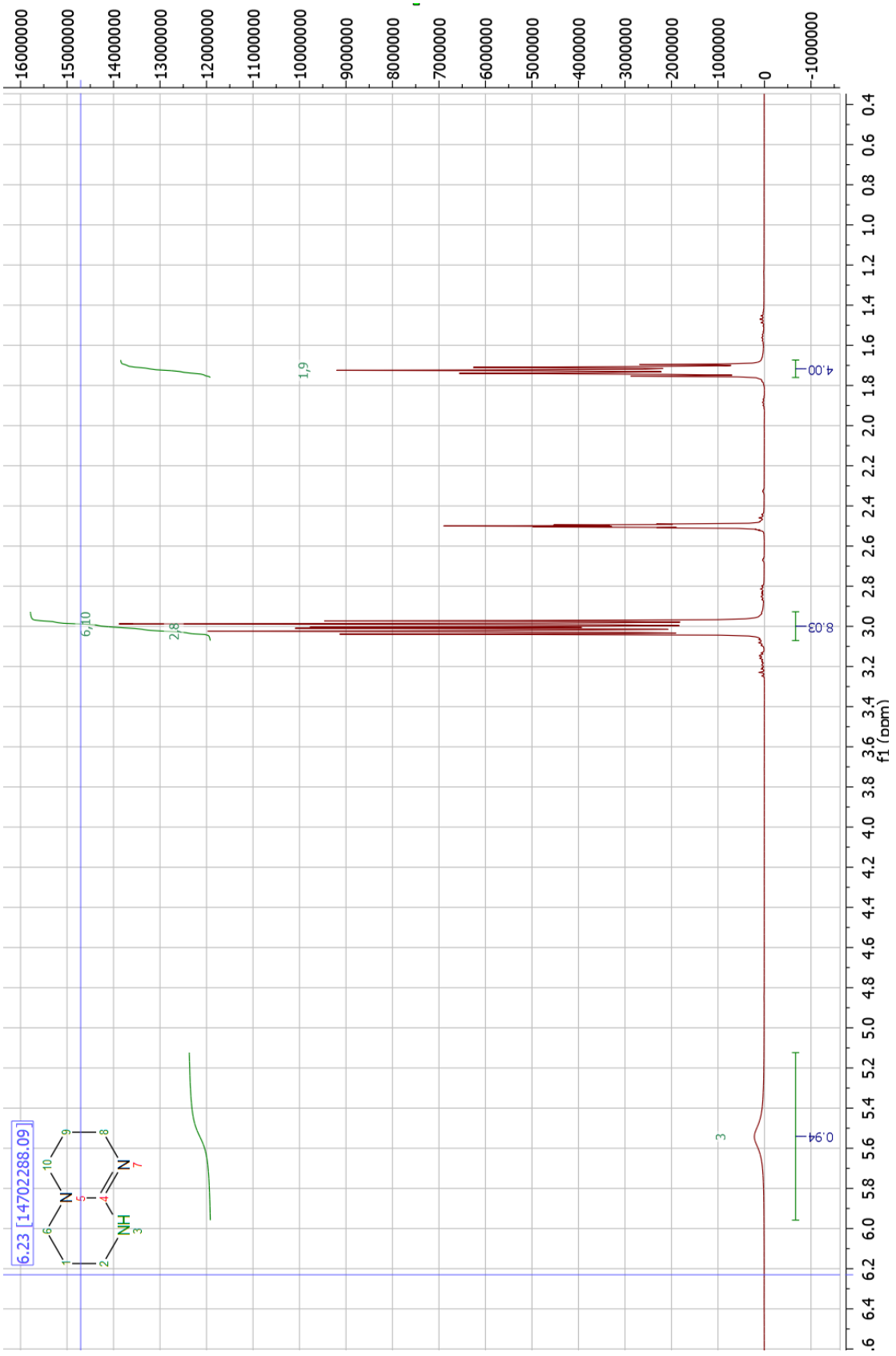

Figure 11. ^{1}H NMR spectra of TBD

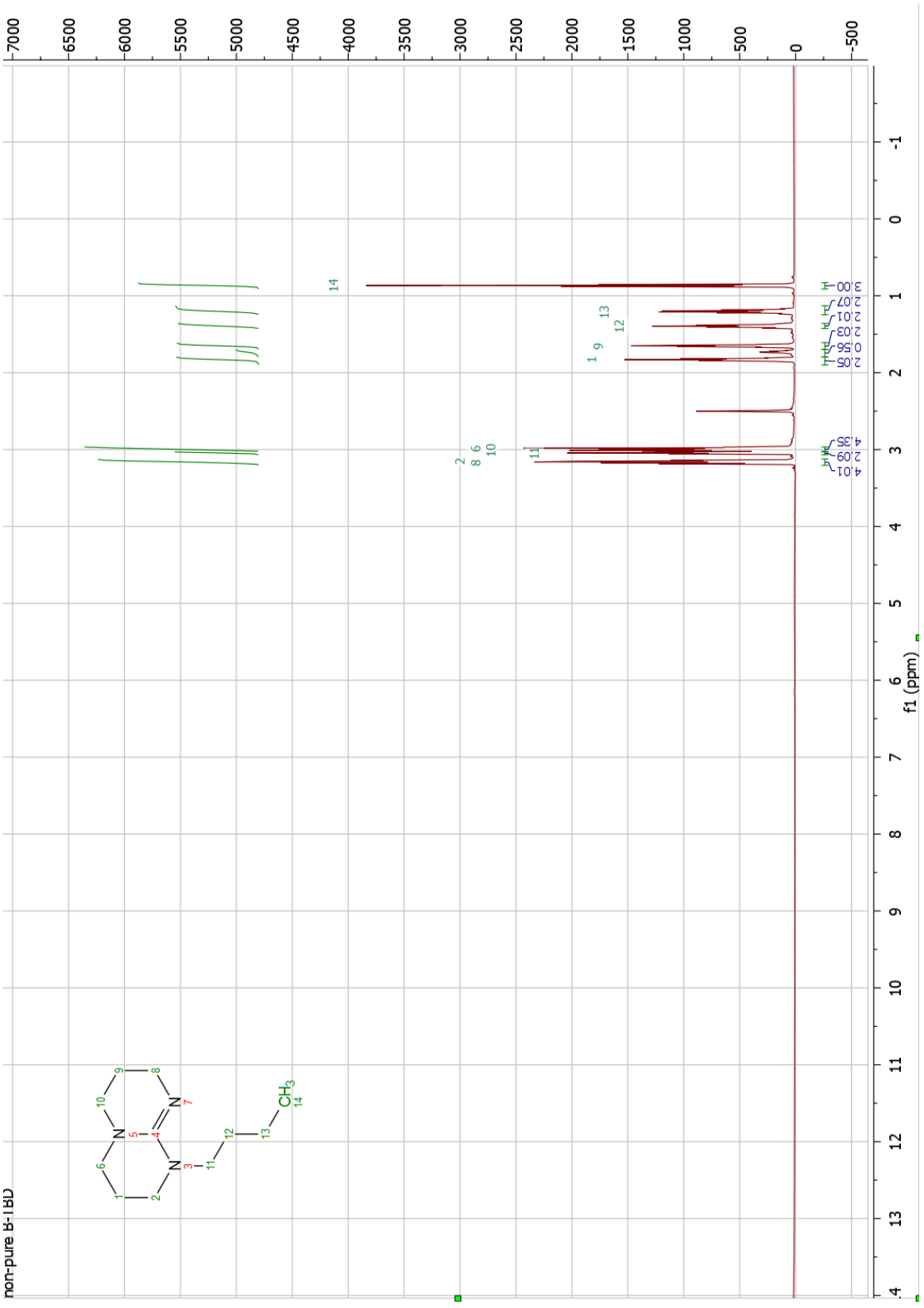

Figure 12. ^{1}H NMR spectra of non-pure b-TBD

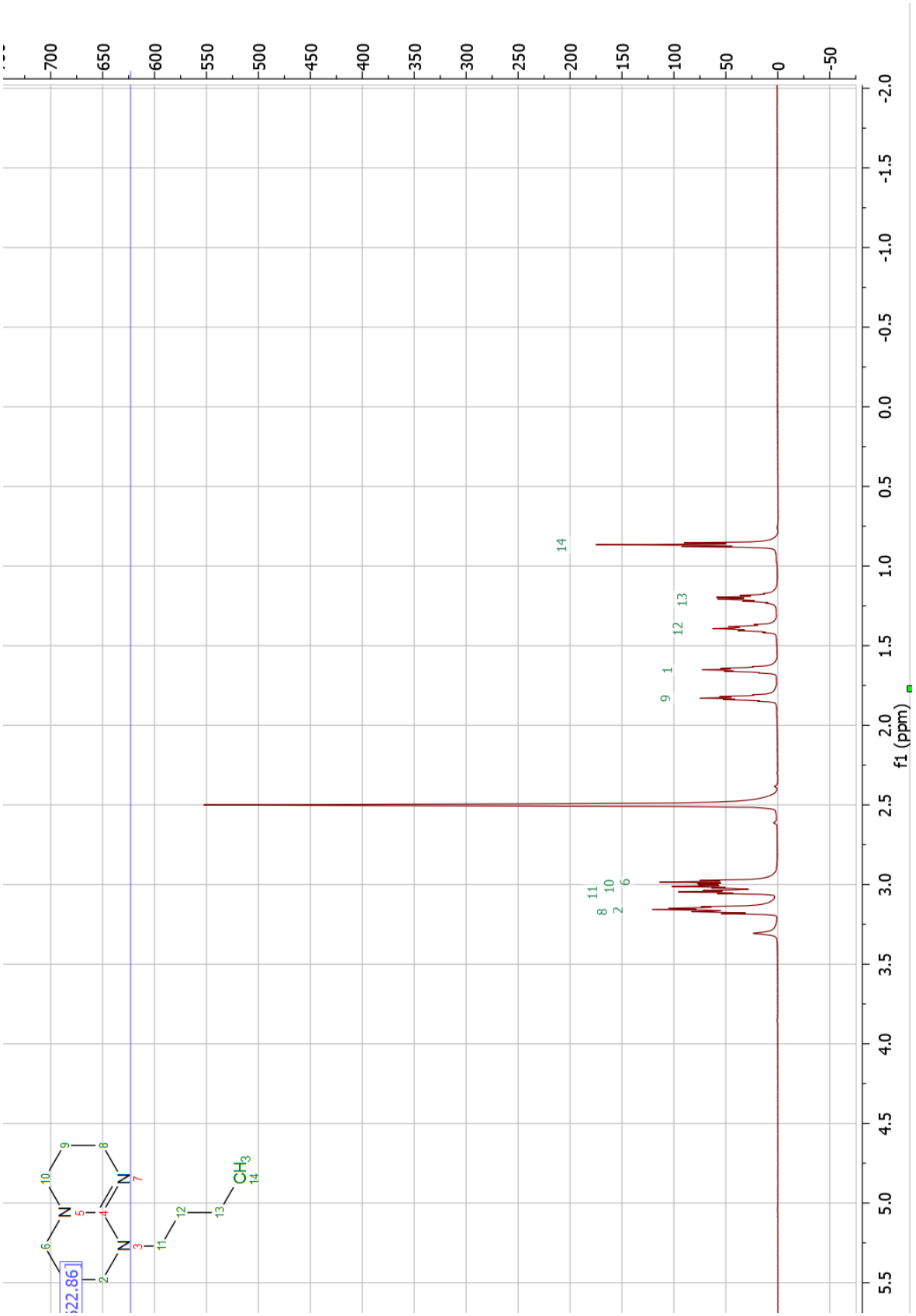

Figure 13. ^{1}H NMR spectra of b-TBD after purification by CO_2

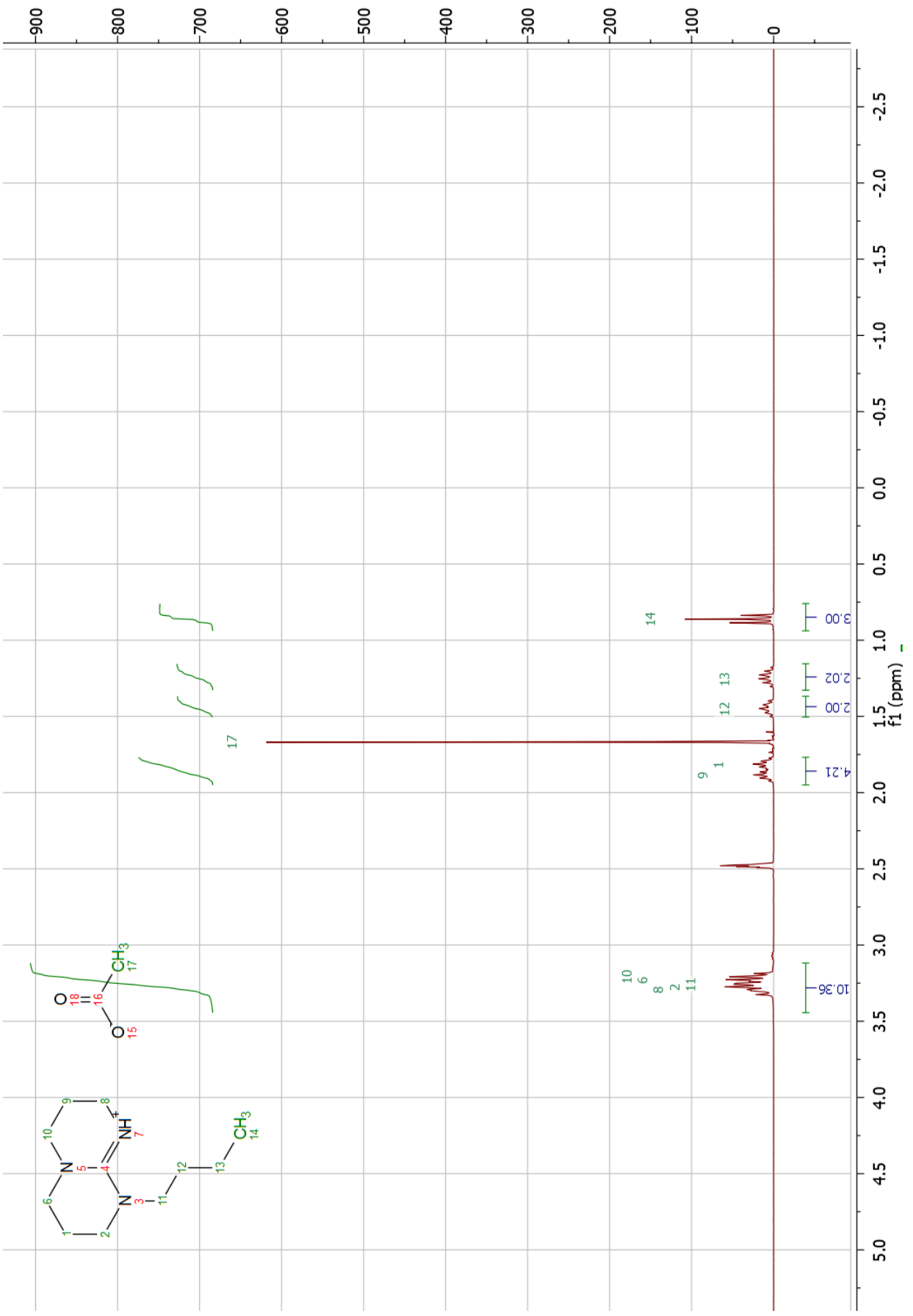

Figure 14. 1H NMR spectra of [b-TBD-H][OAc]

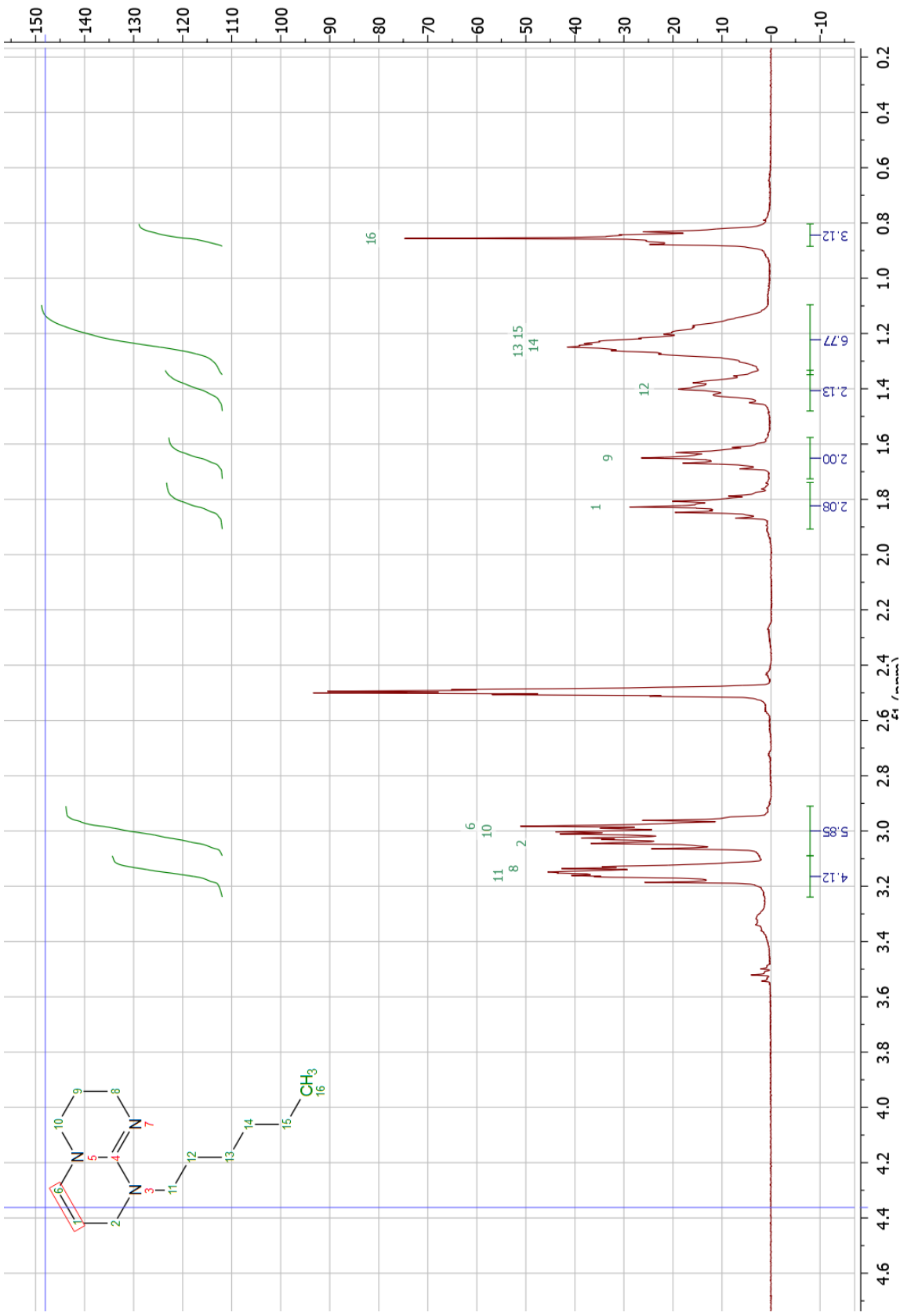

Figure 15. ^{1}H NMR spectra of h-TBD

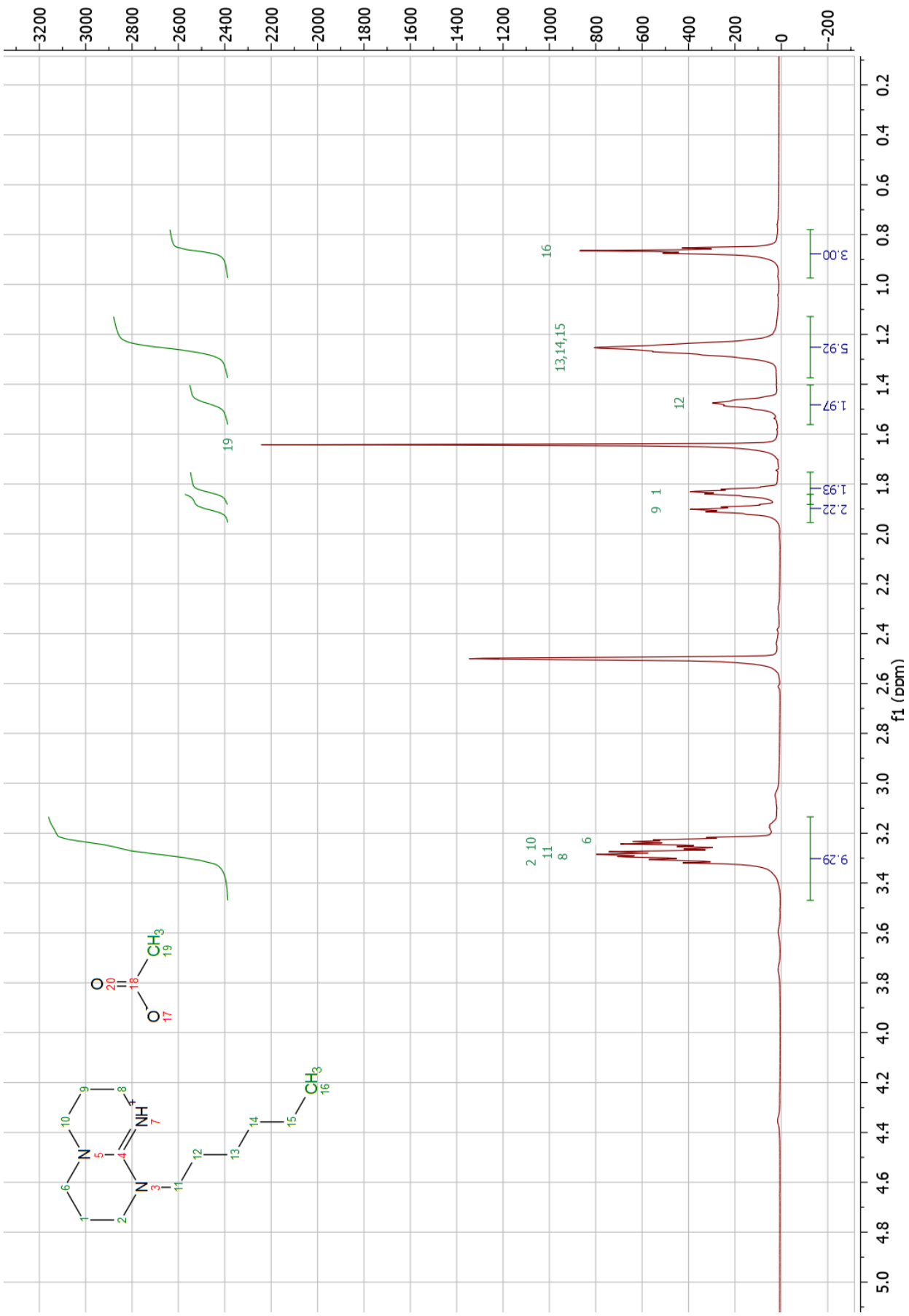

Figure 16. ^{1}H NMR spectra of [h-TBD-H][OAc]

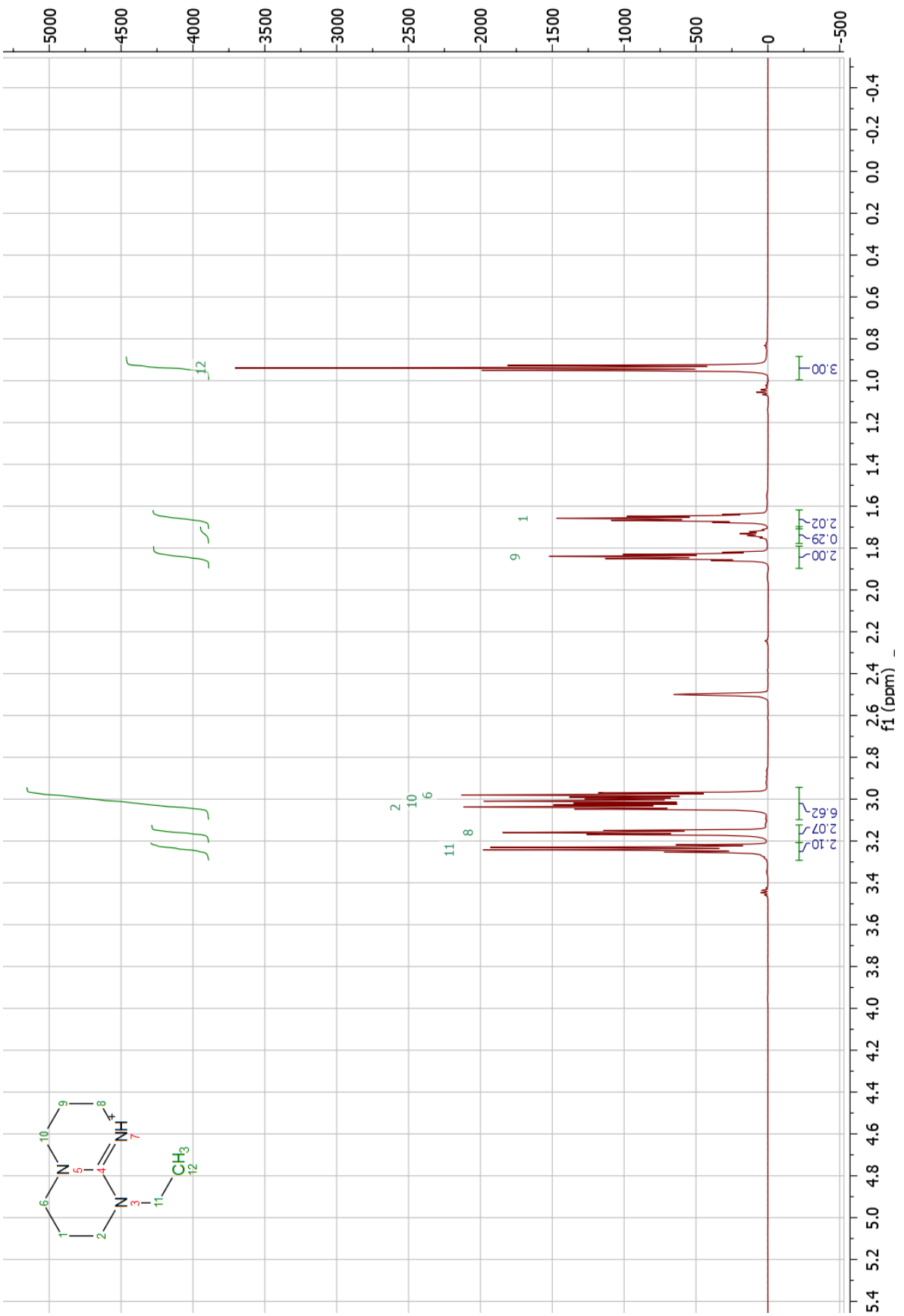

Figure 17. ^{1}H NMR spectra of e-TBD

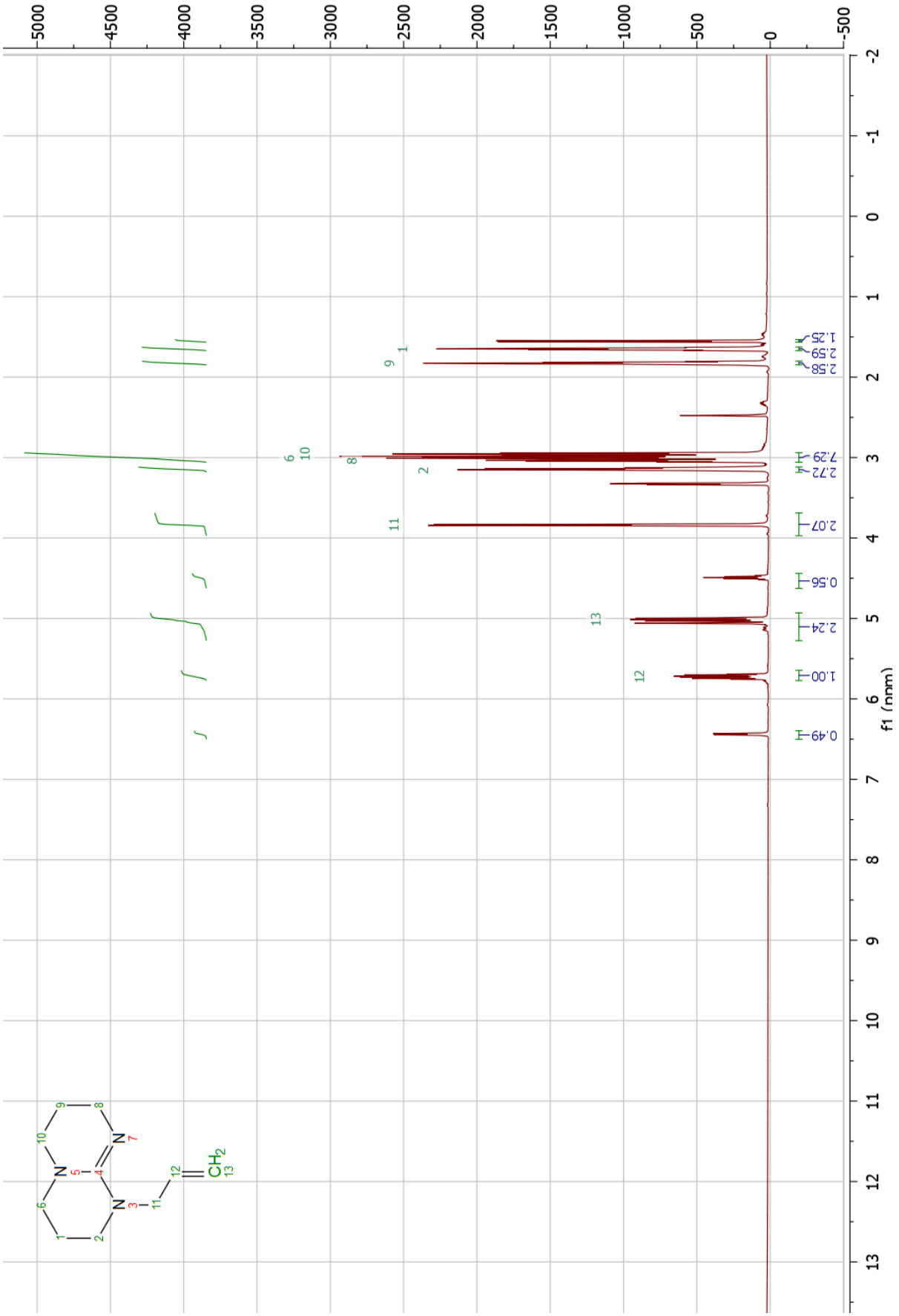

Figure 18. ^{1}H NMR spectra of a-TBD purified by CO_2

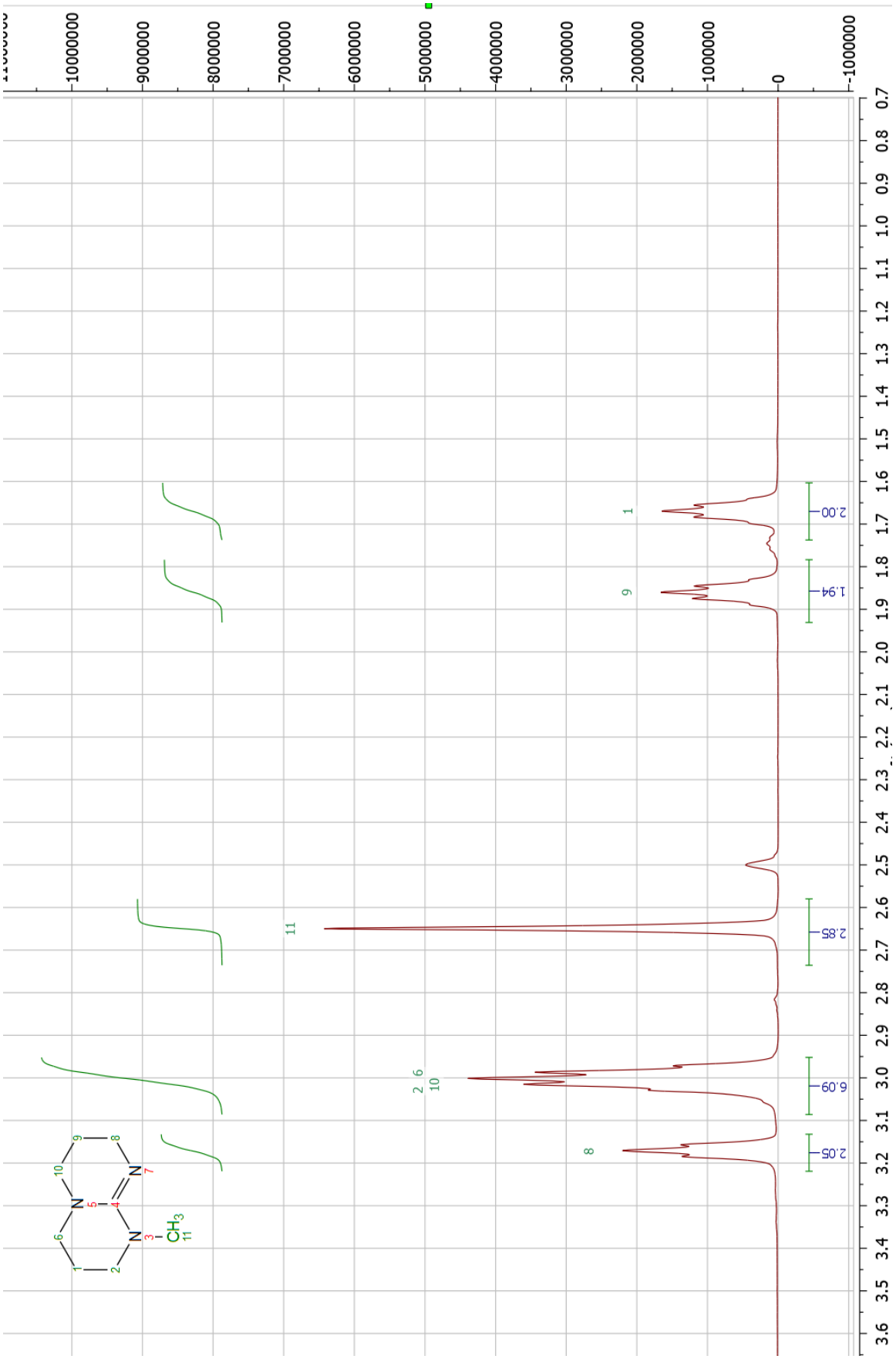

Figure 19. ^{1}H NMR spectra of m-TBD

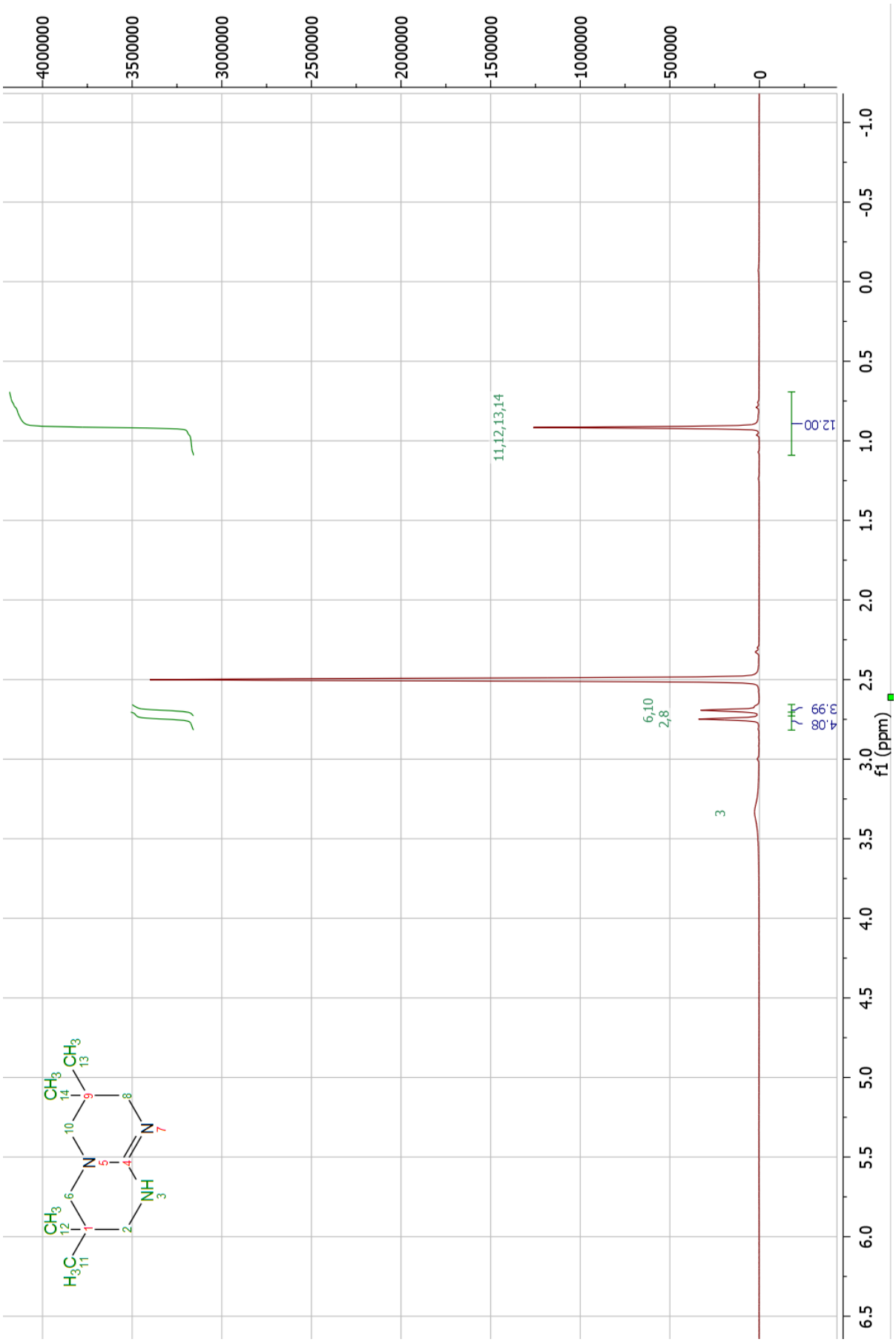

Figure 20. ^{1}H NMR spectra of BTM-TBD

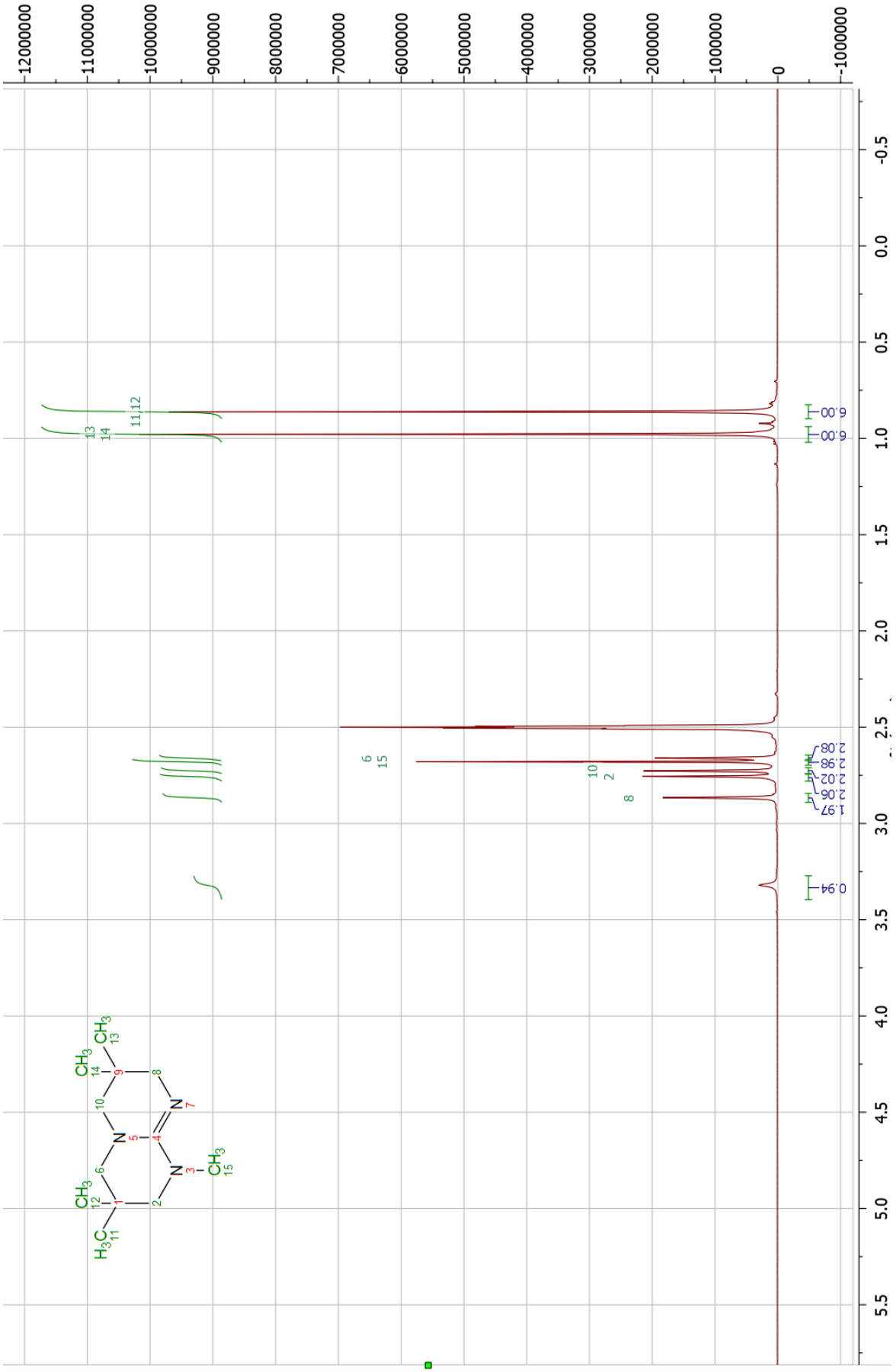

Figure 21. ^{1}H NMR spectra of BTM-mTBD

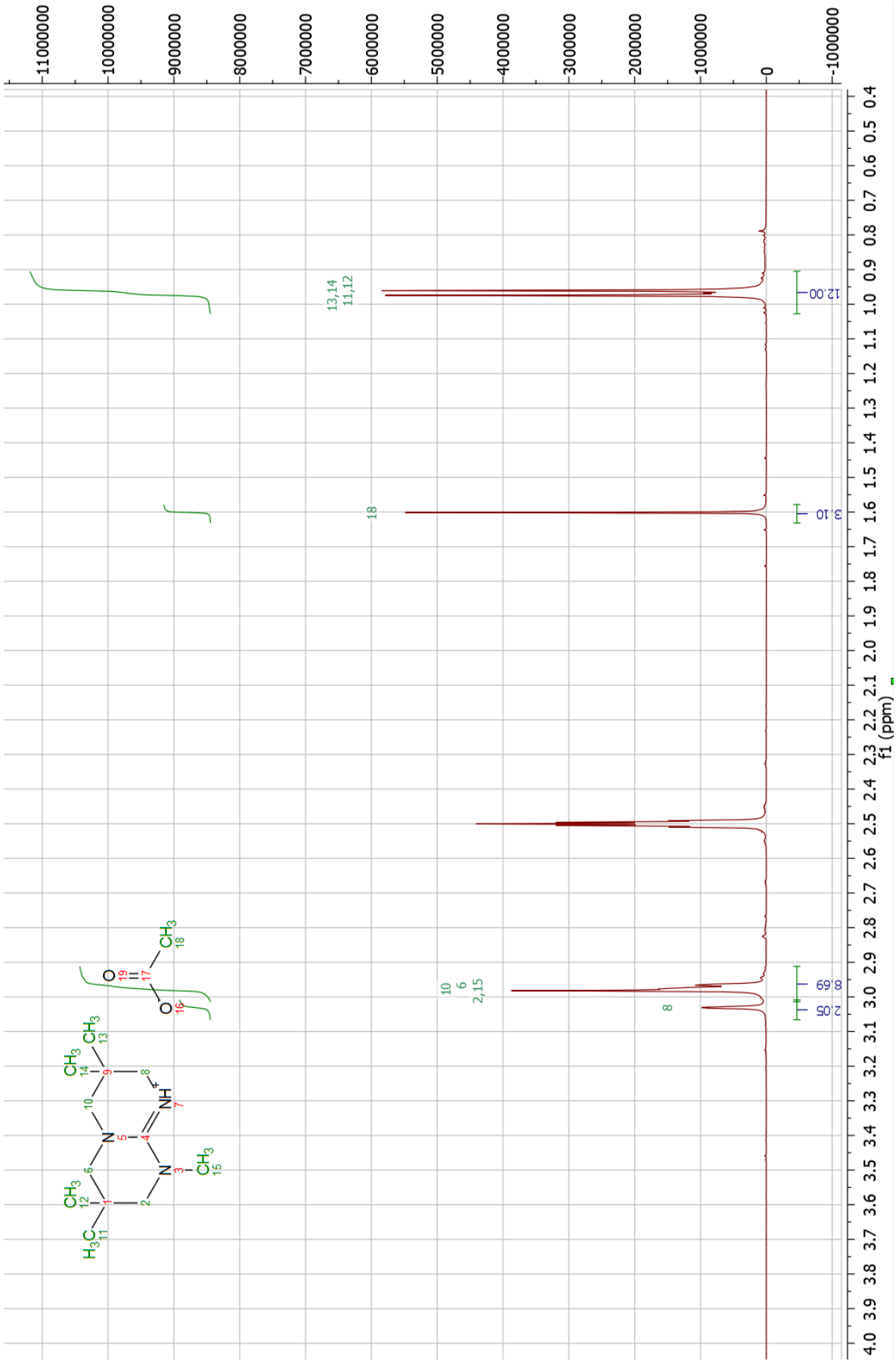

Figure 22. ^{1}H NMR spectra of [BTM-mTBDH][OAc]

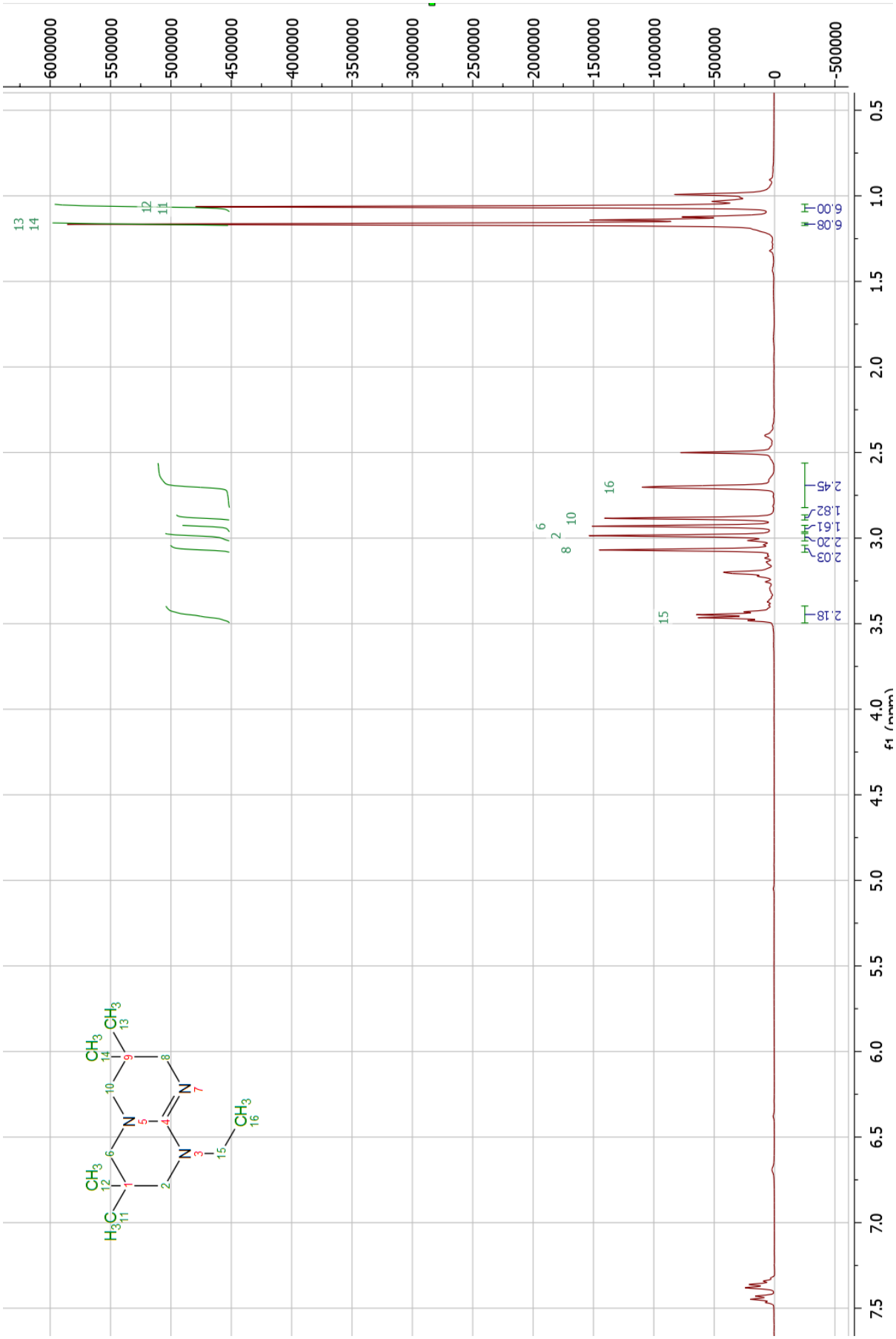

Figure 23. ^{1}H NMR spectra of BTM-mTBD

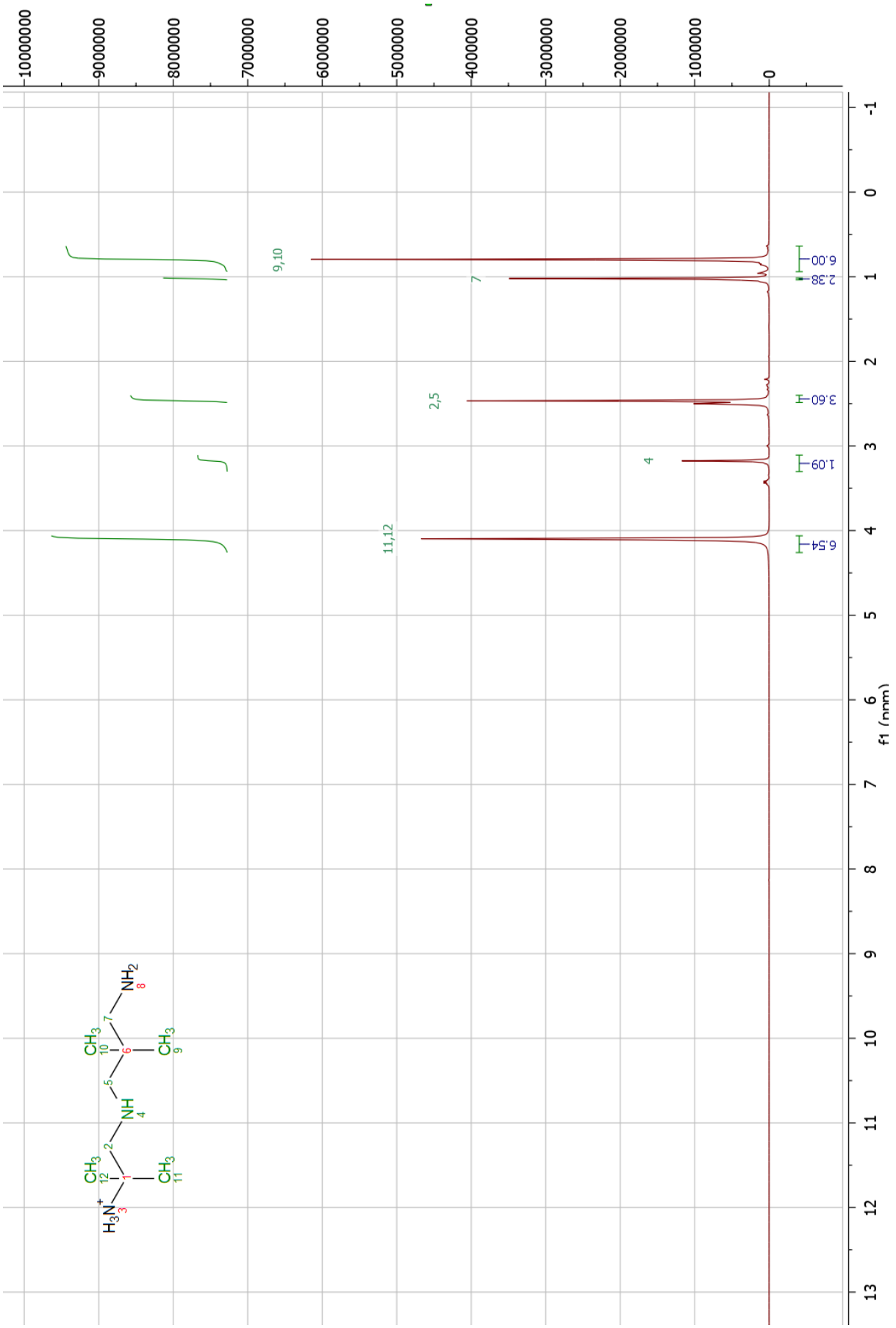

Figure 24. Triamine precursor for TBD derivatives

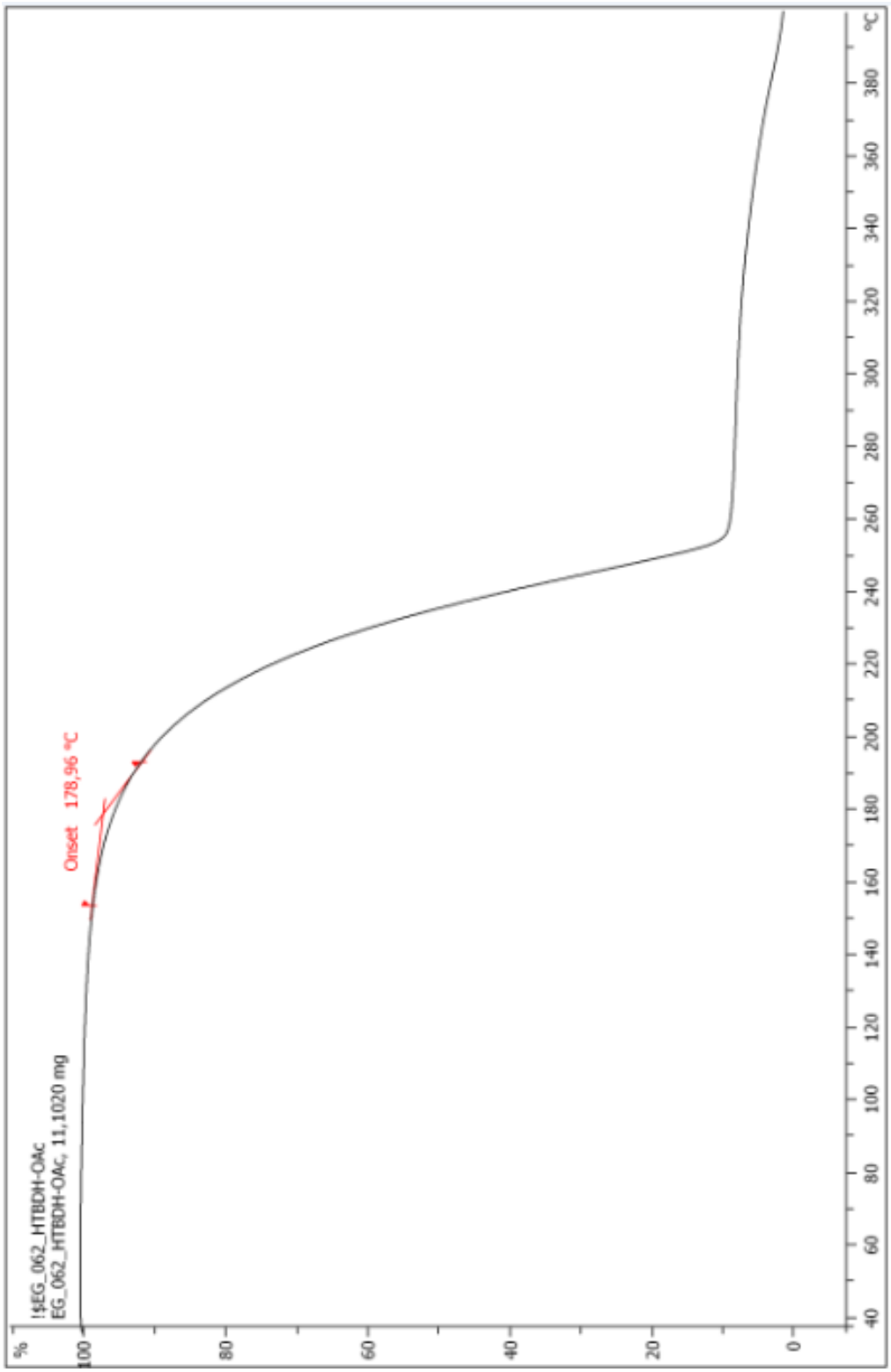

Figure 25. TGA onset of [HTBDH][OAc]

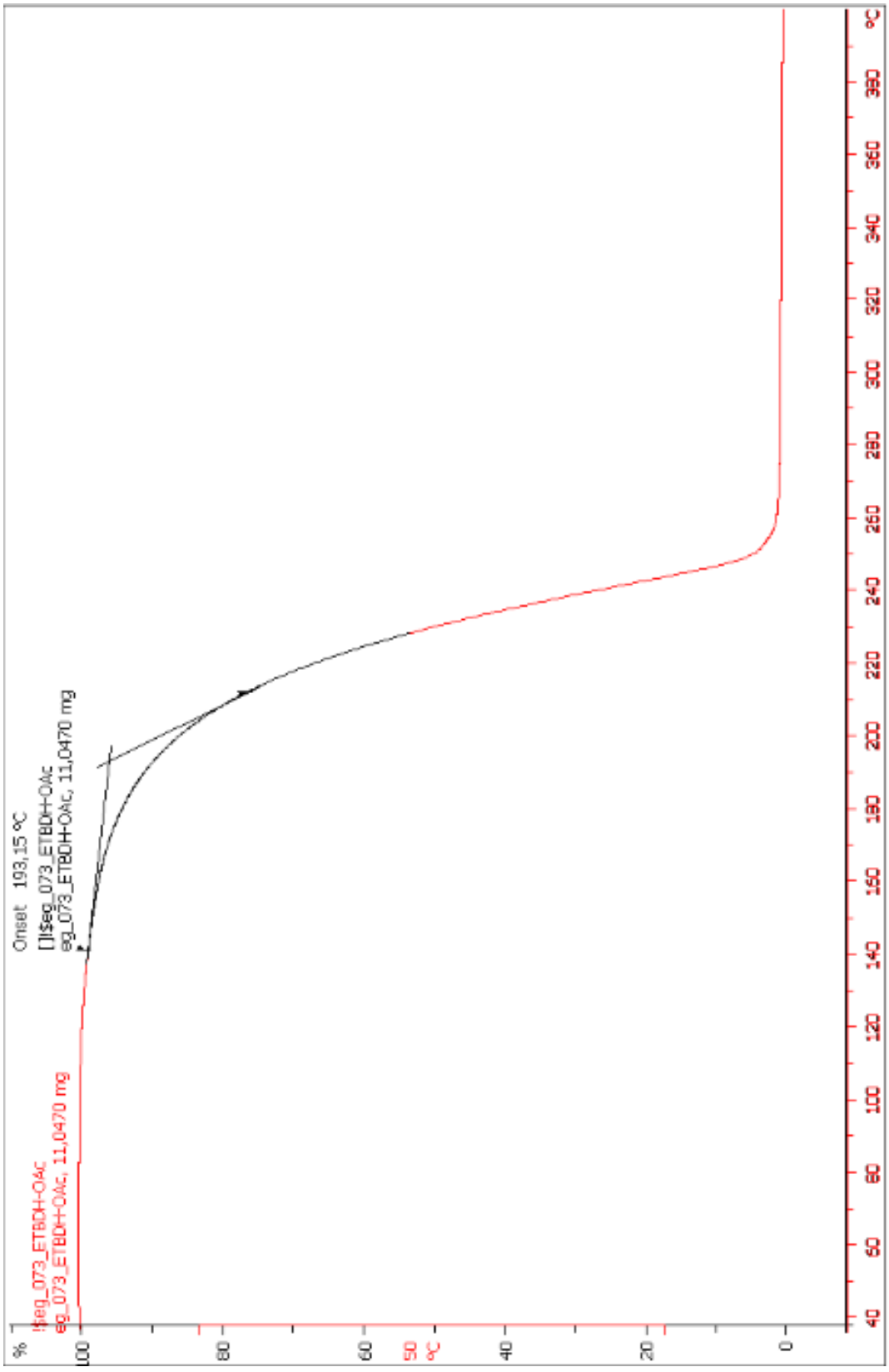

Figure 26. TGA onset of [ETBDH][OAc]

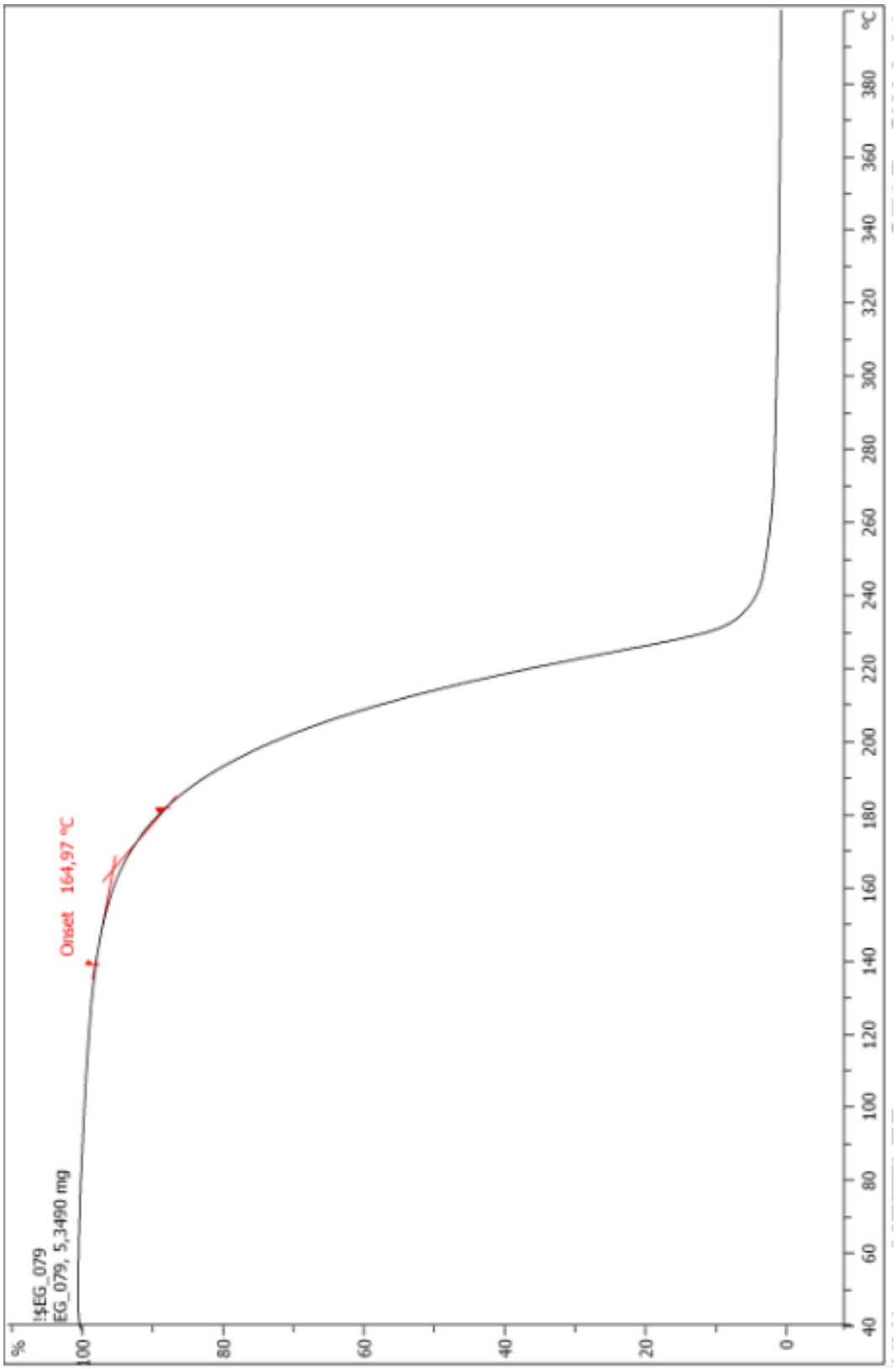

Figure 27. TGA onset of [BTBDH][OAc]

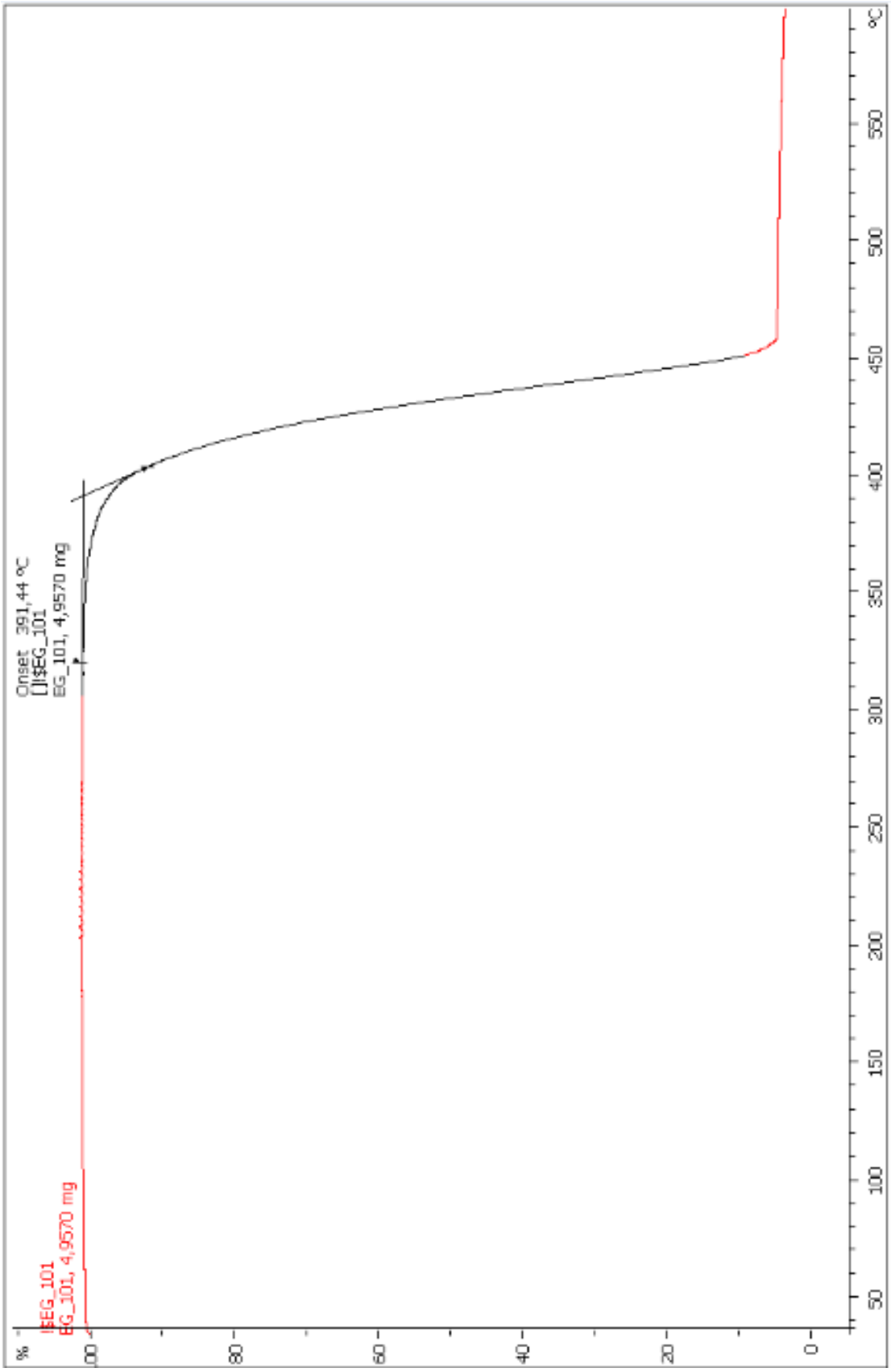

Figure 28. TGA onset of P3FI

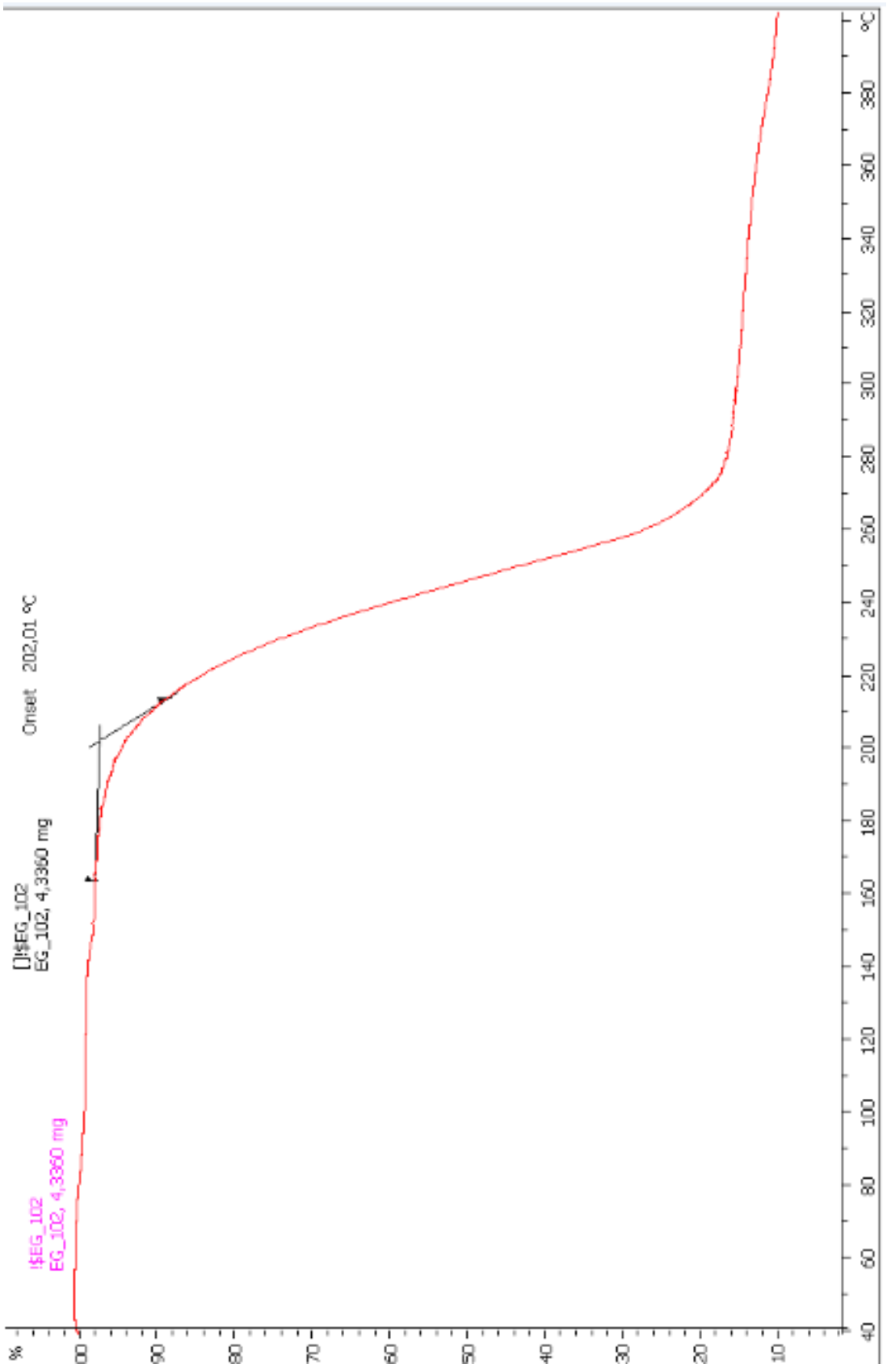

Figure 29. TGA onset of P3FOAc

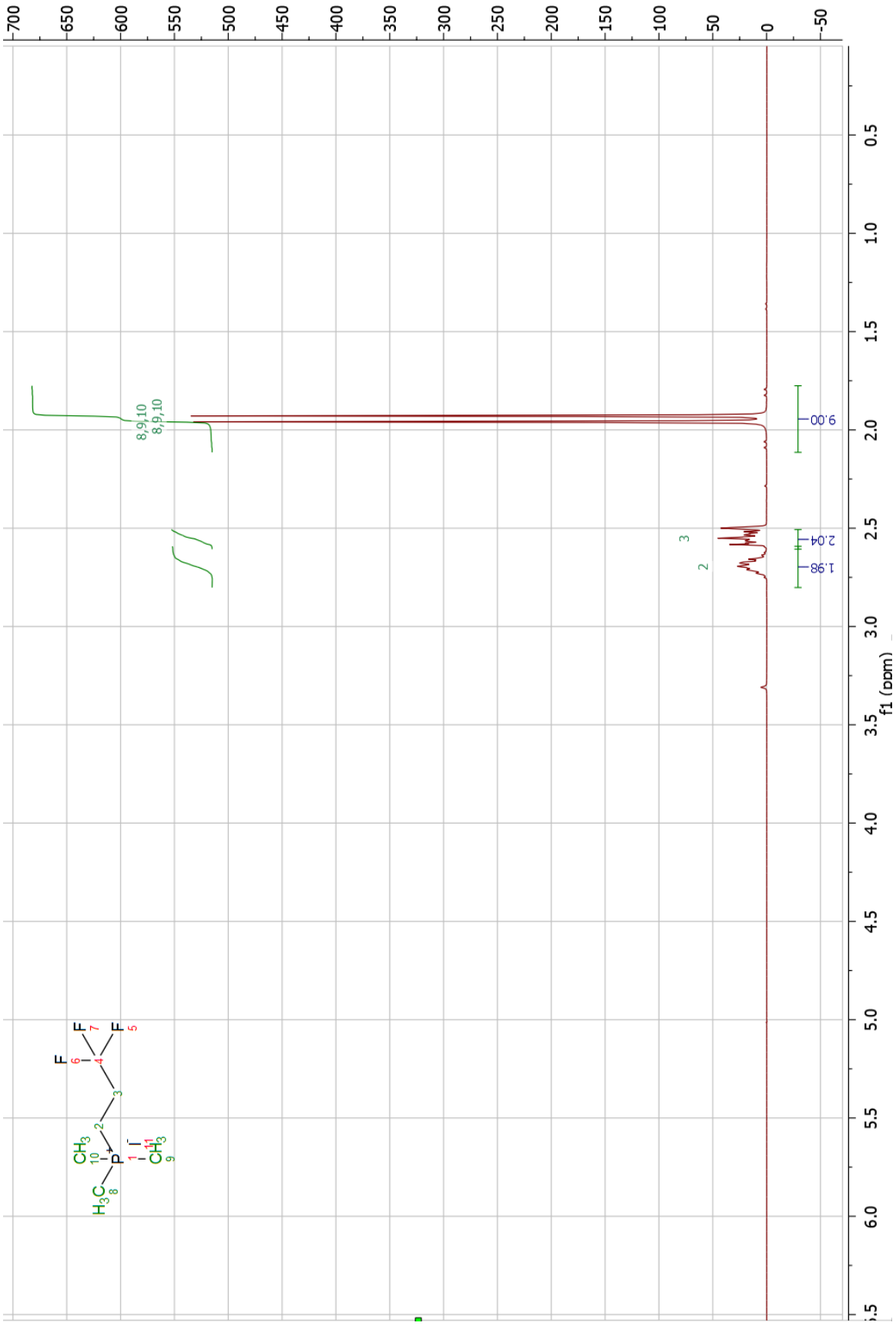

Figure 30. 1H NMR spectra of P3FI in DMSO

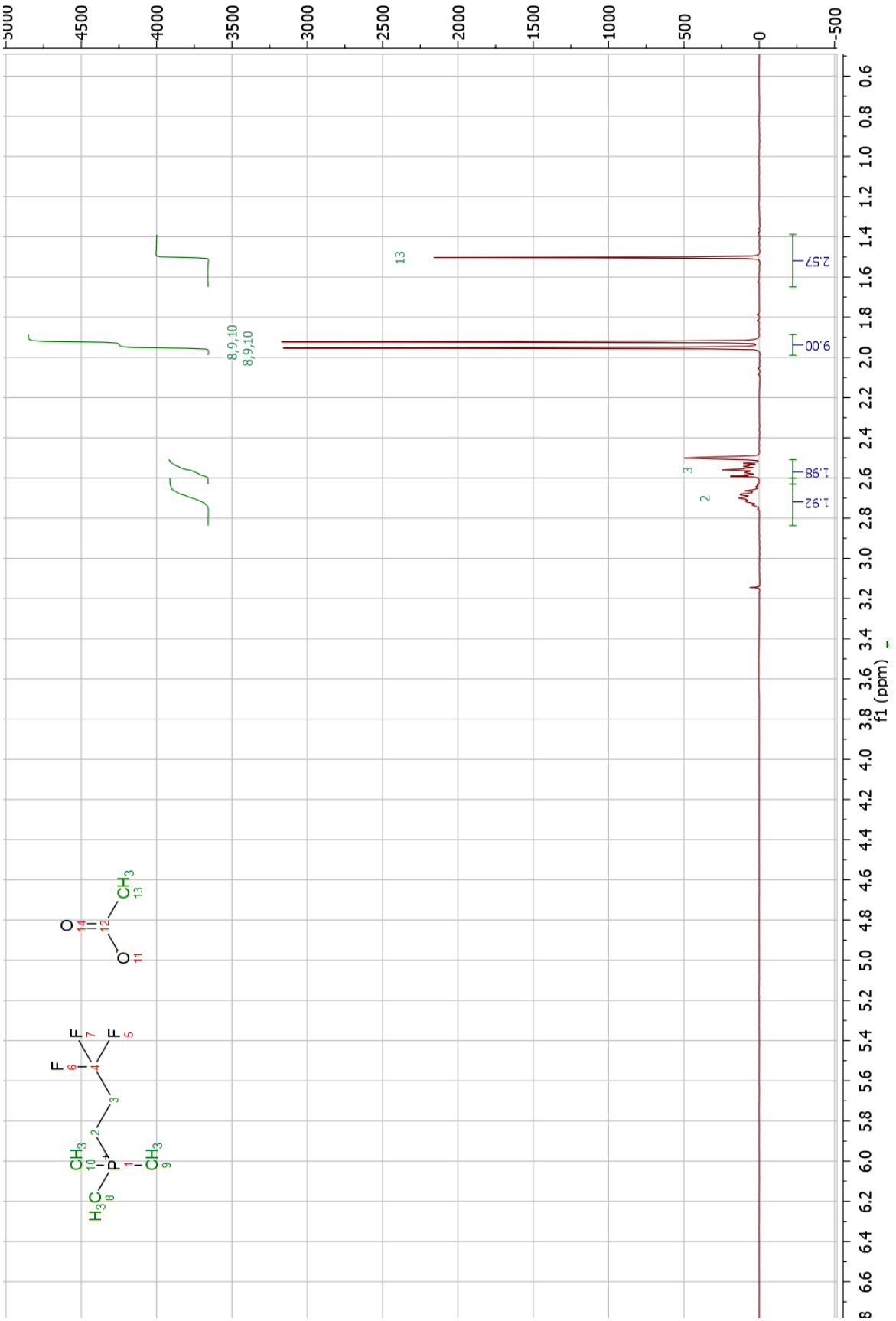

Figure 31. 1H NMR spectra of P3FOAc in DMSO